

Acid catalyst mobility in resist resins

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In a chemically amplified resist absorbed photons generate stable catalyst molecules instead of directly switching resist solubility via photochemical reaction. This allows for much lower exposure doses to be used in imaging. Some catalyst mobility is necessary to achieve amplification since the catalyst must move from reaction site to reaction site, but a mobile catalyst can blur the deposited aerial image. Catalyst molecules that are free to move in exposed regions are also free to move into adjacent unexposed regions. Understanding acid catalyst diffusion in photoresist resins is complicated by the constantly changing chemical environment the diffusing catalyst experiences as the resist undergoes chemical reactions. The diffusing catalyst promotes chemical reactions which change the properties of its surrounding resin. In addition, it is possible a transient material state is generated by volatile reaction byproducts and their desorption from the film. In most photoresist systems it is impossible to separate reaction and diffusion effects. This work describes studies of acid diffusion in polymers that are close structural analogs to reactive photoresist resins but do not react with the diffusing acidic catalyst. The purpose of this study into nonreactive polymer is to gain insight into the more complex, reactive systems. In addition, experiments with polymeric photoacid generators are reported. These materials provide added insight into acid transport in photoresist materials. © 2002 American Vacuum Society. [DOI: 10.1116/1.1523027]

I. INTRODUCTION

Chemically amplified (CA) photoresists achieve high sensitivity by using absorbed photons to generate stable catalyst molecules. These catalyst molecules can then each promote multiple solubility-switching reaction events. A stable catalyst molecule can give high sensitivity, but it also creates the possibility of catalyst migration. Any migration of photogenerated catalyst into adjacent unexposed regions blurs the deposited aerial image. Device feature sizes are decreasing to a point where blurring due to catalyst migration could consume much of the critical dimension error budget. In addition, the stochastic nature of the reaction-diffusion process raises concern that an intrinsic resolution limit is being reached and that current CA photoresist design concepts will be unworkable in the sub-50 nm regime.

This work focuses on “APEX-like” positive tone CA resists. APEX resists were the first successful CA photoresists¹ and most current 248 nm photoresists are derived in part from the APEX system. Even the newer 193 and 157 nm photoresists, while derived from different materials, are very similar in design concept to the original APEX resists. Positive tone CA photoresists undergo a solubility switch by exploiting the acid catalyzed removal of pendant protecting groups from an aqueous base-soluble polymer resin. The protected polymer is insoluble in alkaline aqueous solution, while the unprotected resin is soluble in aqueous base solution. Catalyzed removal of the pendant protecting group switches insoluble to soluble. In the APEX system the polymer resin consists of polyhydroxystyrene with a certain fraction of the phenolic sites protected with an acid-labile *tert*-

butyloxycarboxy (tBOC) protecting group. An onium salt is added as the photoacid generator (PAG). After generation of the photoacid, a postexposure bake is carried out to activate the deprotection reaction in exposed areas. In many resist designs the deprotection reaction results in the generation of small molecule byproducts like carbon dioxide or isobutylene that quickly desorb from the film. Due to the complexity of the reaction-diffusion process it is extremely difficult to develop a full understanding of what is occurring at the molecular level in a baking photoresist. For example, as an acid molecule diffuses, both the reactivity and inherent diffusivity of the surrounding polymer are constantly changing as the exposed areas of photoresist react and change chemical identity. The diffusion coefficient of the acid molecule is certainly a function of bake temperature and local extent of reaction, but it is also possible the resist goes through a transient material state induced by the presence of reaction byproducts in the film. Because temperature, extent of reaction, and byproduct concentration are changing over the course of the bake, the diffusivity of acid molecules is not constant during the postexposure bake.

If the acid diffusion coefficient D_a during the bake was either constant or a simple function of the extent of reaction, solution of the reaction diffusion system would be a straightforward, textbook transport problem. Unfortunately, D_a is not constant and its dependence on extent of reaction is not yet fully understood. Several functional forms are possible to describe the dependence of the acid diffusion coefficient on extent of reaction. For illustration purposes, consider the simple assumption that diffusivity follows a linear mixing rule like the following:

$$D_a = (1 - x)D_{a0} + xD_{af}$$

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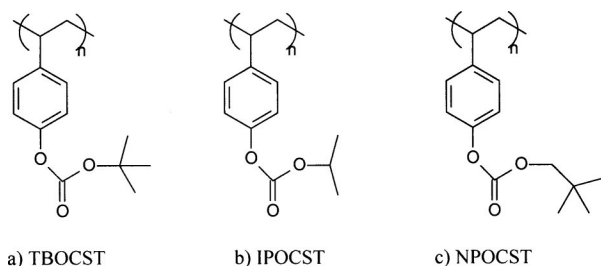


FIG. 1. Structures of analog polymers. Full chemical names: (a) poly(4-*t*-butyloxycarbonyloxystyrene), (b) poly(4-isopropyloxycarbonyloxystyrene), and (c) poly(4-neopentyloxycarbonyloxystyrene).

where x is extent of reaction, D_{ao} is the diffusivity in the unreacted resist, and D_{af} is the diffusivity in the completely reacted resist. D_{af} in an APEX-like resist is simply the acid diffusion coefficient in polyhydroxystyrene (PHS) and is, in principle, measurable. In practice, D_{af} in PHS is so small at typical postexposure bake temperatures (90–130 °C) that it is difficult to directly measure, but it has been measured and reported for certain elevated bake temperatures (165–190 °C).² It is not really possible to directly measure D_{ao} , as it is impossible to prevent reaction while diffusion is measured. Several approaches^{3–5} treat D_{ao} as a fitting parameter in a reaction–diffusion simulation tuned to fit experimental data. This route tends to convolve multiple factors into one number and gives little insight into the process at the molecular level, but can still be useful for process simulation where ease and speed of calculation is paramount. Direct experimental measurement of diffusion coefficients would be ideal but, as mentioned previously, it is not possible in an actual, reactive photoresist material. It is possible to specifically design special “model polymers” or “model acids” that closely mimic most characteristics of the real system while being nonreactive. This approach allows initial diffusivity without reaction to be estimated for an actual system. The use of “model polymers” or “model acids” avoids the uncertainties of data fitting and computer simulation while, of course, bringing other uncertainties into the analysis. Questions of how closely the model system mimics reality are of prime importance. The experimental work reported in this article includes the measurement of acid diffusion coefficients in nonreactive model polymers that are very close structural analogs to protected APEX resin. These data are intended to provide, as directly as possible, estimates of D_{ao} based on experimental results. The polymers used in this work are shown in Fig. 1. Polymer B is poly(4-isopropyloxycarbonyloxystyrene) (IPOCST), and differs from the tBOC-protected PHS (polymer A) by having just one less methyl substituent in the protecting group. Polymer C is poly(4-neopentyloxycarbonyloxystyrene) (NPOCST), and differs from poly(4-*t*-butyloxycarbonyloxystyrene) (TBOCST) by only the inclusion of a methylene spacer unit between the tertiary carbon group and the final oxygen. These polymers are structurally very similar, but they react with acid molecules very differently. TBOCST rapidly deprotects to PHS when heated with even fairly weak acids.

Even the phenol group of PHS is acidic enough to speed the tBOC deprotection reaction.⁶ The isopropyl-protecting group of IPOCST is acid labile, but only with extremely strong acids and at very high temperatures.⁷ Hexafluoroantimonic acid (HSbF_6) catalyzes IPOCST deprotection, but perfluorobutanesulfonic acid ($\text{HSO}_3\text{C}_4\text{F}_9$) does not, even at temperatures up to 180 °C. The neopentyl-protecting group of NPOCST is extremely inert and is entirely unaffected by even HSbF_6 below 185 °C. According to thermogravimetric analysis, NPOCST is thermally stable at temperatures up to at least 250 °C.

Diffusion in these model polymers was measured using a Fourier transform infrared (FTIR) “sandwich” experimental method previously reported.^{2,8} The polymer “sandwich” consisted of three layers: the analyzed model polymer placed between a photoacid feeder layer and an acid detector layer. The stack was created on a mirror backed silicon wafer, which facilitated real-time FTIR monitoring while the sample baked on a hotplate. After the sample was constructed it was exposed to ultraviolet light to generate acid in the feeder layer. When the acid diffused through the middle layer and arrived at the detector layer, a reaction was catalyzed in the detector layer that changed the sample’s IR absorbance. The time to acid arrival at the detector layer provides a transit time which, along with a model polymer layer thickness, can be used to estimate Fickian diffusion coefficients from the relation

$$D \propto L^2/t_{\text{diffusion}},$$

where L is the thickness of the analyzed layer and $t_{\text{diffusion}}$ is acid transit time. This method assumes no significant interaction between the diffusant and its surrounding matrix upsets the random walk nature of the transport process. In actual photoresist systems it is not clear whether the overall reaction–diffusion process is best modeled using Fickian diffusion mathematics, but in nonreactive cases, Fickian diffusion is often applicable. The most difficult problem in reactive systems is understanding how the constantly changing local variables affect acid catalyst diffusivity. Our goal with this work is to fully understand acid diffusion in a simplified model system to gain insight into the much more complex reaction–diffusion systems of real photoresists.

Experiments with polymeric photoacid generators were also performed. These materials are interesting in themselves, but in these reported experiments they are used to provide insight into acid transport in photoresist materials. Two different polymer-bound PAGs were synthesized along with a monomeric version to be used in control experiments. The structures of the three compounds are shown in Fig. 2. In the first polymer-bound PAG, the chromophore is covalently attached to the polymer backbone. Upon exposure, a free acid is generated which is very similar to normal nonpolymeric photoacid generators. The second polymer-bound PAG is the converse of the first, the anionic part of the photoacid generator molecule is covalently linked to the polymer backbone. Upon exposure, this PAG generates acidic molecules that should have extremely restricted mobility as they

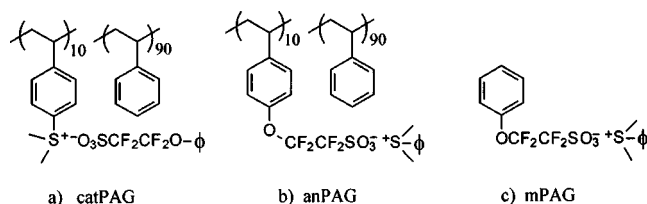


FIG. 2. Structures of polymeric PAGs and the monomeric analog: (a) cation-bound PAG (catPAG); (b) anion-bound PAG (anPAG); and (c) monomeric PAG (mPAG).

are tethered to the polymer backbone. Of interest from the standpoint of understanding acid diffusion is how much reactivity the polymer-bound acid maintains.

II. EXPERIMENT

A. Analog polymers

Poly(4-methoxystyrene) used as the acid generator carrier layer in trilayer experiments was synthesized from the reaction of poly(4-hydroxystyrene), potassium carbonate, and methyl iodide in acetone. The photoacid generator used in trilayer experiments was bis(4-*t*-butylphenyl)iodonium perfluorobutane-1-sulfonate (nonaflate) obtained by donation from Midori Kagaku Co. TBOCST used as the acid detector layer in trilayer experiments was prepared from the polymerization of 4-*t*-butyloxycarbonyloxystyrene monomer using AIBN. This monomer was obtained as a donation from Triquest Chemical Co. IPOCST and NPOCST were prepared by reaction of poly(4-hydroxystyrene) (MW 12 300; Pd 1.93) with the appropriate chloroformate in the presence of triethylamine. The PHS polymer was dissolved in tetrahydrofuran and the chloroformate was diluted in toluene. The polymer-chloroformate mixture was stirred at room temperature overnight (~ 20 h), then neutralized with added base, and precipitated into methanol. Both neopentyl chloroformate and isopropyl chloroformate were purchased from Aldrich Chemical Co. and used as received. The PHS starting material was obtained as a donation from Triquest. The spin-casting solvent for all polymer layers, propylene glycol methyl ether acetate, was also obtained from Aldrich Chemical Co. and used as received. Other aspects of the experimental procedure, such as sample preparation and equipment setup, are the same as reported previously.^{2,8}

Glass transition temperatures were obtained for the IPOCST and NPOCST polymers by means of temperature-scanning spectroscopic ellipsometry. The spectroscopic ellipsometer is a J.A. Woollam M-2000 modified with a heated sample stage. The sample stage was designed in our research group and is controlled with a LABVIEW (National Instruments) program written in house. When measuring glass transition temperatures, the stage temperature was ramped at rate of $5^\circ\text{C}/\text{min}$. The measured T_g s for IPOCST and NPOCST were 88 and 82°C , respectively.

B. Polymeric PAGs

The synthesis of polymeric PAGs required several attempts before workable pathways could be found. A full accounting of the process can be found in Ref. 9. The anionic polymeric PAG was synthesized by copolymerization of the corresponding lithium salt and styrene, followed by metathesis reactions on the resultant copolymer. Most of the workup to the lithium salt has been previously described by Feiring and Wonchoba¹⁰ and Feiring *et al.*¹¹ After polymerization, the product was precipitated into hexanes and washed with water. The polymer was passed through an acidic ion exchange column, then stirred with silver carbonate to convert the polymer to the silver salt. The final product was obtained by addition of thioanisole and iodomethane. Elemental analysis and ^{19}F nuclear magnetic resonance (NMR) were used to confirm the copolymer ratio. For the synthesis of the cationic polymeric PAG (catPAG), the silver salt of the acid anion, along with iodomethane, was mixed with a copolymer of styrene and 4-methylthiostyrene to give the desired product. Shifting of $\text{S}-\text{CH}_3$ resonances in ^1H NMR confirmed total conversion to sulfonium groups had occurred. The monomeric PAG (mPAG) was synthesized by mixing the same silver salt used to make the catPAG with thioanisole and iodomethane, followed by recrystallization from a solution of acetonitrile and diethyl ether.

Two sets of diffusion related experiments were carried out on the polymeric PAGs. In the first experiment the polymeric PAGs were simply blended with TBOCST in a 1:1 mass ratio, while the mPAG was blended with TBOCST to give acid molar loading that was closely equivalent to loading of the polymeric PAGs. Phase compatibility when blending polymers is always a concern, but the spin cast films of these solutions formed acceptable films from solutions that were slightly hazy. After spin casting films, the samples were postapply baked at 90°C for 90 s, then exposed to ultraviolet light to generate acid. The samples were then placed on a 90°C hotplate and monitored by FTIR. The disappearance of the carbonyl peak from TBOCST was monitored to determine the extent of reaction. The second diffusion experiment involved a variation on the previously mentioned "sandwich" experiment. Instead of a trilayer film stack only two layers were used: a film of pure polymeric PAG and the TBOCST detector layer. This is equivalent to watching the spread of acid from a sharp, printed feature edge. The amount of reaction in the TBOCST film can be used to estimate the acid diffusion distance if a relatively sharp reaction/diffusion is assumed. Films were postapply baked at 90°C for 90 s. The upper TBOCST layer was applied by a previously reported film-floating method.⁸ Films were exposed to ultraviolet light, then placed on a 90°C hotplate and monitored by FTIR.

III. RESULTS AND DISCUSSION

A. Analog polymer acid diffusivity

The goal of this work was to obtain an estimate of D_{ao} in TBOCST by measuring D_a in nonreactive analog polymers.

As seen in Fig. 1, the model polymers are structurally very close to TBOCST, but often small structural differences can make a large difference in chemistry. In most aspects, other than response to acid, these analog polymers appear to be fairly similar to TBOCST. All three polymers have similar solubility in the solvents THF, toluene, and PGMEA, and are insoluble in water, methanol, and hexane. All three polymers contain a carbonate group, and have almost indistinguishable IR spectra. The glass transition temperatures do differ somewhat, especially between the model compounds and TBOCST. The glass transition temperatures of IPOCST and NPOCST are both in the range between 80 and 90 °C, while the glass transition of TBOCST has been measured by ellipsometry as 120 °C. The differences in glass transition temperature mean it is not reasonable to directly take values of D_a measured in the model polymers at any given temperature as the estimate of D_{ao} at that same temperature. Since the glass transition has a large impact on diffusivity in polymers, the correct analogy between D_a and D_{ao} would be to use equivalent differences in polymer glass transition temperature and bake temperature, or a reduced temperature. For example, the estimate for D_{ao} at 105 °C (15 °C below TBOCST T_g) would come from IPOCST D_a at 73 °C (15 °C below IPOCST T_g).

The IPOCST polymer is probably as close to TBOCST as any possible polymer while still being unreactive with perfluorobutanesulfonic acid under normal postexposure bake conditions. IPOCST reacts with some strong acids, but it requires much harsher conditions than those used in this study. The lesser reactivity of IPOCST results from the lesser stability of the carbocation that must be formed as the isopropyl group is cleaved. The deprotection reaction of IPOCST goes through a secondary carbocation intermediate while TBOCST goes through a more stable tertiary carbocation. The NPOCST polymer is also close structurally to TBOCST, but its chemistry is not as close as IPOCST. Under harsh conditions IPOCST eventually deprotects, whereas NPOCST is extremely inert. NPOCST is even more stable because it must go through a primary carbocation intermediate, which is even less stable than the secondary carbocation of IPOCST. Lesser stability of the intermediate translates into lower probability of formation, which translates into less reactivity.

Figure 3 shows the measured diffusion coefficients for IPOCST and NPOCST over the temperature range 65–95 °C. Nominal film thickness for IPOCST was 150 nm, while the film thickness for NPOCST was 320 nm. As temperature traverses the glass transition region for these polymers, it is expected that D_a will change dramatically. IPOCST measured D_a s range in magnitude from 10^{-14} cm²/s at the lowest temperature to 10^{-12} cm²/s at the highest temperature. As seen in Table I, IPOCST seems to have a comparatively fast diffusion rate at the glass transition temperature. Measured D_a s for NPOCST cover the same magnitude range as IPOCST but diffusion in NPOCST is generally slower at every temperature despite NPOCST's lower glass transition temperature. As seen in Table I, NPOCST has acid

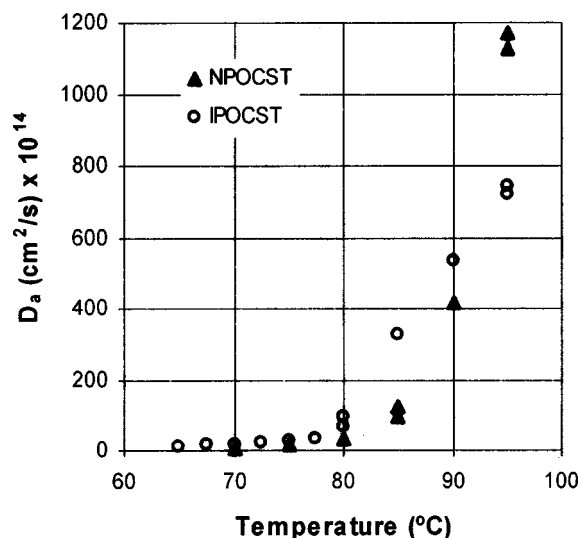


Fig. 3. Measured acid diffusion coefficients for IPOCST and NPOCST polymers ($1 \text{ nm}^2/\text{s} = 10^{-14} \text{ cm}^2/\text{s}$).

diffusion rates that are more in line with the previously measured polymers PHS and poly(ethyl methacrylate).

As stated previously, the goal of this work is to provide estimates for acid diffusion coefficients in reactive TBOCST polymer films. Table II gives estimates for the initial diffusivity D_{ao} of TBOCST based on measured values from the two analog polymers. When values from both polymers are available an average value is also reported. Estimated values from the isopropyl polymer are on average larger than the neopentyl polymer by almost a factor of 5. Researchers at IBM have reported diffusion coefficients for the same acid (perfluorobutanesulfonic acid) in TBOCST at temperatures in the range of 65–105 °C.⁵ Their estimates range from 5×10^{-16} cm²/s at 65 °C up to 1.5×10^{-13} cm²/s at 105 °C. At the only point of overlap (105 °C) in the two data sets, the D_{ao} estimate from IPOCST is 1.3×10^{-13} cm²/s, while the average estimate is smaller by only a factor of 2. The IBM estimate comes from simulation fits to experimental results, but seems to be in good agreement with our independently determined estimates. Another estimate from simulation fits to experimental data comes from Zuniga and Neureuther, who measured diffusion in APEX-E and report an

TABLE I. Acid diffusivity measured in polymers near T_g . *PEMA = poly(ethylmethacrylate).

$T - T_g$ (°C)	D_a (cm ² /s) IPOCST	D_a (cm ² /s) NPOCST	D_a (cm ² /s) PHS ^a	D_a (cm ² /s) PEMA ^b
10		6.1×10^{-12}	1.3×10^{-12}	1.1×10^{-12}
5	3.7×10^{-12}	1.4×10^{-12}	4.3×10^{-13}	1.8×10^{-13}
0	2.7×10^{-12}	6.0×10^{-13}	1.3×10^{-13}	3.5×10^{-14}
-5	1.6×10^{-12}	2.0×10^{-13}	3.3×10^{-14}	1.6×10^{-14}
-10	3.5×10^{-13}	9.2×10^{-14}	—	3.4×10^{-15}
-15	1.3×10^{-13}	2.5×10^{-14}	—	—
-20	8.8×10^{-14}	—	—	—

^aReference 1.

^bReference 7.

TABLE II. Estimated TBOCST acid diffusivity as function of temperature.

Temperature (°C)	D_{ao} (cm ² /s) (IPOCST)	D_{ao} (cm ² /s) (NPOCST)	D_{ao} (cm ² /s) (average)
130	—	6.1×10^{-12}	—
125	3.7×10^{-12}	1.4×10^{-12}	2.6×10^{-12}
120	2.7×10^{-12}	6.0×10^{-13}	1.7×10^{-12}
115	1.6×10^{-12}	2.0×10^{-13}	9.0×10^{-13}
110	3.5×10^{-13}	9.2×10^{-14}	2.2×10^{-13}
105	1.3×10^{-13}	2.5×10^{-14}	7.8×10^{-14}
100	8.8×10^{-14}	—	—

initial diffusion coefficient of 5.6×10^{-14} cm²/s at 90 °C as a fitting parameter.¹² The comparison here is not direct as APEX-E consists of only partially protected PHS polymer and the acid structure is not reported and is not likely the same as our experiments. Other researchers have reported diffusion coefficients in TBOCST in the temperature range 90–130 °C for perfluorooctanesulfonic (PFOS) acid,¹³ rather than the perfluorobutanesulfonic (PFBS) acid used in these experiments. PFOS acid is a rather larger molecule than PFBS acid, and the reported diffusion coefficients reflect this as they range for PFOS from 2.6×10^{-16} cm²/s at 90 °C to 1×10^{-14} cm²/s at 130 °C, approximately 2 orders of magnitude smaller than PFBS.

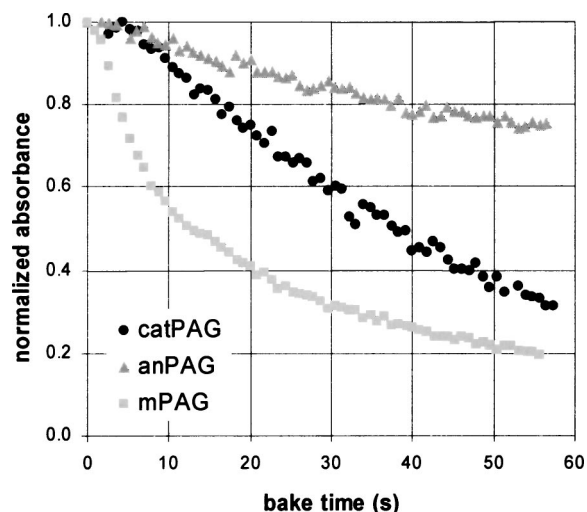
Several diffusion models have been employed to explain experimental observations in CA resists. At short times (less than 2 min) the rate of linewidth spreading can seem almost constant and a single constant diffusion coefficient can be used to model the entire reaction–diffusion process. Over longer times the diffusion rate slows down dramatically and the diffusion coefficient used to explain the short time behavior does not adequately explain the long time behavior. Some have postulated acid loss mechanisms, such as base trapping or acid evaporation, to account for the apparent time dependent behavior of diffusion coefficients. Others have tried to account for the change in diffusion coefficient by taking into account the material change that occurs during the postexposure bake. Zuniga *et al.*³ and Zuniga and Neureuther¹² proposed several models with diffusion coefficients dependent on extent of reaction. Others have found that using different diffusion coefficients for reacted and unreacted material is necessary to fit experimental data.⁵ The acid diffusion coefficients for pure TBOCST from Table II would tend to overestimate diffusion distances observed in real photoresists. For example, a diffusion coefficient with magnitude 10^{-13} cm²/s results in acid movement of over 100 nm during the course of a 60 s postexposure bake. The actual linewidth spread observed in experiment and manufacturing is usually much less than this. Of course, the diffusion coefficient of the unreacted material is not the only factor controlling blurring. In many resists the reacted material will have a much lower diffusivity than the initial material and this will help to limit diffusion. Several methods for accounting for extent of reaction and material change have been proposed, including a simple linear mixing rule and free volume dependent models. We have previously proposed a reaction front model to

account for observed transport behaviors. In the reaction front model, reaction effects like byproduct formation temporarily enhance acid mobility before diffusion slows to the reacted material rate. It is not yet clear which model is correct, but the estimated D_{ao} for TBOCST, while large enough to give approximately correct diffusion lengths, are not large enough to match the initial diffusion rates that have been observed.⁸ To match these initial rates some reaction enhanced diffusion seems necessary if our estimates for D_{ao} in TBOCST are correct.

B. Polymeric PAGs

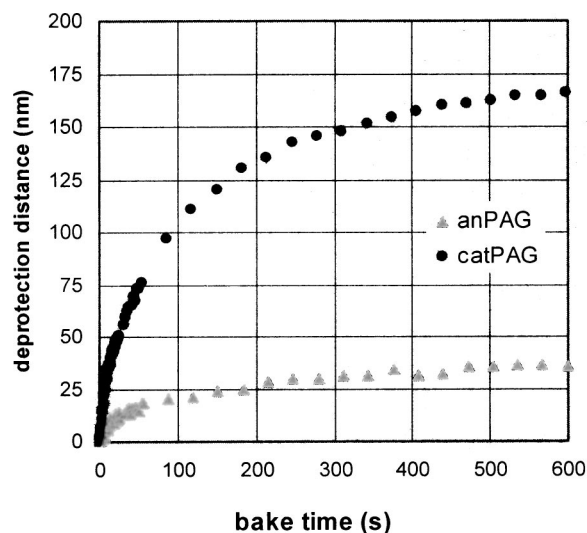
The polymeric PAGs are interesting materials with multiple potential uses. A cationic-bound PAG like the one shown in Fig. 2 has the potential to limit outgassing during exposure since the volatile piece (the aromatic ring) of the chromophore is covalently attached to the polymer backbone. It has been shown that much of the material outgassed during exposure consists of PAG chromophore fragments generated by photodecomposition.¹⁴ These cationic-bound polymeric PAGs could drastically reduce the potential for outgassing. The anionic-bound PAG does not have any mechanism to limit outgassing as the chromophore is not covalently linked to the polymer backbone, but it does have a mechanism to greatly reduce acid diffusion. Any generated acid will have its conjugate base, or counteranion, covalently attached to a polymer backbone. In effect, the acid has an extremely bulky conjugate base and long distant migration will be extremely difficult. Due to Coulombic forces, separation of the proton and its conjugate base is also severely limited in material with dielectric constants of most photore-sist polymers.¹⁵ Tethering the conjugate base to the polymer backbone restricts the radius over which a generated acid molecule can exert influence during the course of the postexposure bake. While the polymeric PAGs have some advantages, as currently constructed these polymeric PAGs have several limitations. Synthesis is tedious, especially for the anion-bound PAG. The current PAGs are polystyrene copolymers and the miscibility of the PAG with common photore-sist resins is a problem. The range of possible copolymers is also limited due to the synthetic route. The PAGs, as currently synthesized, also appear to have poor storage stability. Both polymeric PAGs decomposed to generate significant amounts of acid after storage at room temperature over the course of about 6 months. The mPAG does not seem to have a stability problem. The activation energy for thermolysis of the PAGs is under investigation.

Two sets of diffusion experiments were carried out with the polymeric PAGs. In the first experiment the PAGs were simply mixed with TBOCST and cast as films on to silicon wafers. There was some evidence of phase separation in the films after spin casting. After exposure the films were baked and extent of reaction was monitored in real time by FTIR. Results for the three PAG materials are shown in Fig. 4 and are in line with expectations. The mPAG generated the fastest deprotection rate and the greatest extent of reaction, while the polymer with attached PAG cations approached the ex-

FIG. 4. Blend experiment with PAGs in TBOCST ($T=90\text{ }^{\circ}\text{C}$).

tent of reaction of the unbound PAG. The polymer with attached PAG anions was much less reactive than either of the other two PAGs. While the monomeric PAG and the cation-bound PAG generate the same acid it is not really surprising that the polymeric PAG should appear somewhat less reactive. It is likely that some of the acid generated in the cation-bound PAG system is segregated in polystyrene rich areas. Before reaction can occur the acid must diffuse into areas with reactive units. The anion-bound PAG generates an acid with a counteranion covalently bound to the polymer backbone, so in addition to generating acid in nonreactive polystyrene rich regions, the mobility of the acid is extremely restricted. These films were exposed with very high doses of ultraviolet light to minimize effects caused by differences in quantum efficiency. No attempt was made at full characterization of the optical properties of the polymeric PAGs.

In the second set of experiments, bilayer film stacks were studied. Films of pure polymeric PAG were cast, and then a layer of TBOCST was placed on top. After exposure the films were baked and extent of reaction was monitored in real time by FTIR. Experimental results for the two polymeric PAGs are shown in Fig. 5. The mPAG is not shown because a suitable carrier film could not be found to allow spin casting. When the mPAG is added to polystyrene in a 1:9 molar loading (acid:polystyrene unit) the film drastically phase separates, and proper films cannot be formed. Results from the bilayer experiments are shown as diffusion distance versus bake time. The stated diffusion distances assume that the reaction and diffusion fronts are colocated and relatively sharp. The distance reported for the unbound acid (catPAG) is approximately 160 nm over the course of a 10 min $90\text{ }^{\circ}\text{C}$ bake. This is some 100 nm longer than reported⁸ for $\text{HO}_3\text{SC}_4\text{F}_9$ (PFBS), but the generated acid in this case is the slightly lighter $\text{HO}_3\text{SC}_2\text{F}_4\text{OC}_6\text{H}_5$. The slight difference in molecular weights is probably only part of the reason for the differences in diffusion distance, it is possible the phenyl group of $\text{HO}_3\text{SC}_2\text{F}_4\text{OC}_6\text{H}_5$ enhances solubility in the resist

FIG. 5. Bilayer experiment with polymeric PAGs ($T=90\text{ }^{\circ}\text{C}$).

resin, perhaps even acts as a plasticizer to promote diffusion into the film. The results from the bound acid are slightly surprising. With the acid counteranion bound to the polymer backbone, it was expected that diffusion would be extremely restricted; perhaps only to the distance the acidic proton can separate from its counteranion. Results from these bilayer experiments suggest a diffusion distance of 25 nm. This distance is much too great to be accounted for by just proton separation from the counteranion as the force required to separate the charge over that distance would be impossibly large. Some diffusion of the entire acidic polymer is necessary to explain a deprotection distance of 25 nm or another explanation must be found. One explanation for the observed results is that the two layers are intermixing during sample preparation. This seems unlikely because the polymers are not extremely phase compatible to begin with and the sample preparation method is designed to limit opportunities for mixing between layers. Another explanation is perhaps the polymeric acid is actually penetrating into the upper layer due to reaction enhanced diffusion. At the initial stages of the bake the sample is in an unusual state, the presence of reaction byproducts like carbon dioxide and isobutylene, perhaps along with photolysis fragments from the PAG chromophore, could create a severely plasticized film stack that could temporarily allow for interpenetration of the polymers in the upper and lower layers. It is also possible that some sort of free acid was generated from the PAG by an unexpected, undetermined pathway.

IV. CONCLUSIONS

Acid diffusion coefficients for the TBOCST analog polymers IPOCST and NPOCST have been experimentally determined over temperature ranges near their glass transition temperatures. These results allow acid diffusion coefficients for TBOCST homopolymer to be estimated over the temperature range $100\text{--}130\text{ }^{\circ}\text{C}$. Estimates provided by the ana-

log polymers are in close agreement with estimates provided by other researchers using different methods for determination. Experiments with polymeric PAG materials show that they are photoactive, and generate acid that behaves qualitatively as expected. The cation-bound PAG produces an acid that behaves very much like a typical, monomeric PAG. The anion-bound PAG gives an acid with a very low diffusion distance, if somewhat greater than expected. These PAGs will be useful for a number of fundamental studies and with modification could potentially be useful industrially.

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