

# The Multifunctional Role of Base Quenchers in Chemically Amplified Photoresists

Adam R. Pawloski, Christian, and Paul F. Nealey\*

Center for Nanotechnology and Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

Received February 26, 2002. Revised Manuscript Received July 29, 2002

A systematic investigation of four base quenchers in chemically amplified photoresist revealed that the role of the base quencher is more complex than rapid, stoichiometric neutralization of photoacid. The base quenchers studied included common supplements to chemically amplified photoresist, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-piperidineethanol (1PE), and tetrabutylammonium hydroxide (TBAH), and an atmospheric contaminant and poison to chemically amplified resists, *N*-methyl pyrrolidinone (NMP). Acid–base neutralization, deprotection, and development processes in formulations with and without base quencher were evaluated to determine the effects of the base quencher on resist processing. The extent of deprotection of the polymer was measured by infrared spectroscopy and analyzed as a function of the concentration of photoacid within the resist. The concentration of photoacid after exposure was determined using a standard addition technique that quantified the efficiency of photoacid generation. Dissolution rates were measured as a function of the extent of deprotection, and the induction time during development was measured as a function of the resist dissolution rate. Some base quenchers were found (i) to neutralize photoacid in the resist with less than stoichiometric proportions, (ii) to act as dissolution inhibitors or promoters, and (iii) to lengthen the induction time during development. These results show that base quenchers act in considerably more complex ways than the stoichiometric neutralization of photogenerated acid, and understanding these multifunctional characteristics is important for the design of improved resist systems for high-resolution lithography.

## Introduction

The process of photolithography that is used to pattern the many layers of modern microelectronic devices is currently capable of printing features with dimensions <100 nm in thin films of chemically amplified photoresist.<sup>1</sup> To continue to push this resolution limit to even smaller dimensions, new photoresist materials must be developed and their formulations optimized for each exposure technology. To do so, the performance of the photoresist must be understood from the contributions of its constituent components to the chemical processes that lead to image formation.

Although first conceptualized for imaging with deep ultraviolet light,<sup>2</sup> chemically amplified resists are now used for all advanced exposure tools, from ultraviolet light to electron beams. The principal components of a chemically amplified resist are a polymer and a photoacid generator (PAG). Upon exposure to radiation, the PAG decomposes to generate a photoacid. The photoacid diffuses within the photoresist film during a postexposure bake (PEB) and catalyzes chemical reactions that alter the development rate of the film. Chemical am-

plification is derived from the fact that one molecule of acid may catalyze many reactions. The extent of reaction is controlled by the concentration of photoacid generated upon exposure and the PEB conditions. In the case of positive tone resists, photoacid catalyzes the removal of blocking groups (e.g., *tert*-butoxycarbonyl) on the polymer. Removal of these blocking groups deprotects hydrophilic sites (e.g., hydroxyl) on the polymer, increasing the dissolution of the resist film in a developer solution, typically aqueous base. A pattern in the resist film is then obtained by exploiting the difference in dissolution rates of the exposed and unexposed regions.

Resist formulations often contain additives other than the protected polymer and PAG to improve performance. Some additives may promote adhesion, increase mechanical strength, or inhibit the dissolution of unexposed resist. Strong bases, referred to as base quenchers, are often added to enhance pattern resolution.<sup>3,4</sup> The addition of base improves resist contrast and line width control by (i) neutralizing acid that is generated in the dark regions of the pattern by diffraction effects (or by the intensity threshold for X-ray or phase shifted masks) and (ii) eliminating excessive diffusion of photo-

\* To whom correspondence should be addressed. E-mail: nealey@engr.wisc.edu.

(1) Nalamasu, O.; Houlihan, F. M.; Reichmanis, E.; Cirelli, R.; Timko, A. *Polym. Mater. Sci. Eng.* **2001**, *84*, 207.

(2) Ito, H.; Willson, C. G. *Org. Coat. Appl. Polym. Sci. Proc.* **1983**, *48*, 60–64.

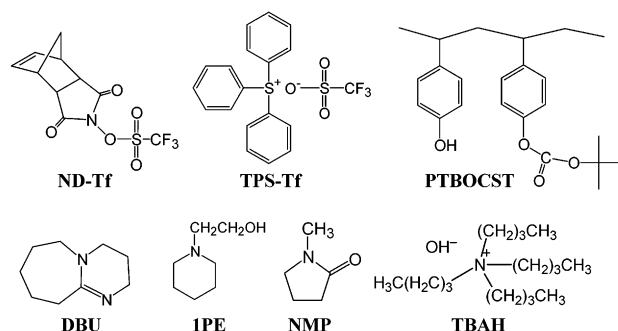
(3) Hinsberg, W. D.; Houle, F. A.; Sanchez, M. I.; Morrison, M. E.; Wallraff, G. M.; Larson, C. E.; Hoffnagle, J. A.; Brock, P. J.; Breyta, G. *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, *3999*, 148–160.

(4) Houlihan, F. M.; Person, D.; Rushkin, I.; Dimov, O.; Reichmanis, E.; Nalamasu, O. *J. Photopolym. Sci. Technol.* **2001**, *14*, 373–384.

acid from the exposed regions into the unexposed regions. Some amount of acid diffusion is undoubtedly necessary for chemical amplification; however, excessive acid diffusion blurs the image of the printed feature.

We, along with others, have previously used base quenchers as analytical reagents within photoresist films for the quantification of photoacid generation efficiency.<sup>5–9</sup> This technique is similar to a standard addition experiment in which the concentration of an unknown is determined by adding known quantities of an analyte to the system and measuring some analytical response. The increase in the response with concentration of the analyte allows the concentration of the unknown to be determined. As applied to resist films, base quenchers can be used as the analyte to determine the concentration of photogenerated acid using resist development as the analytical detector. Since the base neutralizes photogenerated acid, the exposure dose required to generate a given concentration of photoacid within a resist increases as the concentration of base added to the resist increases. Likewise, the exposure dose necessary to develop the resist film increases as the base concentration increases since the dissolution of the resist depends on the concentration of photoacid remaining after neutralization with base. Experimental data for the increase in exposure dose required to develop the resist as a function of the added base concentration is then fit to a model to extract the efficiency of photoacid generation (*C* parameter<sup>10</sup>) for the resist. The model assumes that the base quencher acts only to neutralize a stoichiometric amount of photoacid before the postexposure bake and has no other effect on the development or deprotection of the resist. In previous work, this assumption was validated for a system using 1-piperidineethanol (1PE) as the base quencher in a photoresist consisting of norbornene dicarboximidyl triflate (ND-Tf) as the PAG in a matrix of poly(*p*-*tert*-butoxycarbonyloxystyrene-*co-p*-hydroxystyrene).<sup>6</sup> For this system, resist formulations with and without base quencher exhibited the same dissolution behavior and dependence of deprotection on the concentration of photoacid. These results verified that 1PE acted within the resist only to neutralize photogenerated acid and validated the application of the standard addition model to this system. To our knowledge, this is the only resist system for which the assumptions of the standard addition technique have been fully tested and validated.

Whether to be used as additives or analytical reagents in photoresist films, the role of the base quencher must be understood for its impact on image formation. Key issues include the extent of the neutralization reaction



**Figure 1.** Chemical structure of the components used in this work. Photoacid generators: norbornene dicarboximidyl triflate (ND-Tf) and triphenylsulfonium triflate (TPS-Tf). Base quenchers: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-piperidineethanol (1PE), *N*-methyl pyrrolidinone (NMP), and tetrabutylammonium hydroxide (TBAH). Polymer: poly(*p*-*tert*-butoxycarbonyloxystyrene-*co-p*-hydroxystyrene) (PTBOCST).

between photoacid and base and any changes in the dissolution properties of the resist (inhibition, promotion, or induction time effects) that may arise due to the incorporation of the base into the resist formulation. In this work, we investigate the role of the base quencher on dissolution and deprotection processes in chemically amplified resist. The standard addition technique was used to quantify the efficiency of photoacid generation in these resist systems, enabling deprotection of the resist to be analyzed as a function of the concentration of photoacid generated upon exposure. Four base quenchers were selected: a strong amine base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), a weaker amine base, 1-piperidineethanol (1PE), a strong ionic base, tetrabutylammonium hydroxide (TBAH), and a weakly basic amide, *N*-methyl pyrrolidinone (NMP). The bases DBU, 1PE, and TBAH have previously been incorporated into photoresist solutions, and NMP is known to be an atmospheric contaminant and poison to chemically amplified resists.<sup>11,12</sup> Each base was characterized in resist systems using two different photoacid generators, norbornene dicarboximidyl triflate (ND-Tf) and triphenylsulfonium triflate (TPS-Tf). The polymer for all resists studied consisted of poly(*p*-*tert*-butoxycarbonyloxystyrene-*co-p*-hydroxystyrene) (PTBOCST). The chemical structures for these resist components are shown in Figure 1.

The role of base quenchers in chemically amplified resist was determined to impact resist performance in ways beyond the stoichiometric neutralization of photo-generated acid. Depending on the composition of the base quencher, processes including the incomplete neutralization of photoacid, dissolution inhibition, dissolution promotion, and an increased induction time during development were observed in the resist systems studied in this work. Comparing these effects for systems containing two different photoacid generators indicated that the incomplete neutralization of photoacid by the base was affected by the composition of the PAG. The process of dissolution inhibition and an

(5) Cameron, J. F.; Fradkin, L.; Moore, K.; Pohlers, G. *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, 3999, 190–203.

(6) Pawloski, A. R.; Christian, Nealey, P. F. *Chem. Mater.* **2001**, 13, 4154–4162.

(7) Pawloski, A. R.; Szmanda, C. R.; Nealey, P. F. *Proc. SPIE-Int. Soc. Opt. Eng.* **2001**, 4345, 1056–1065.

(8) Szmanda, C. R.; Brainard, R. L.; Mackevich, J. F.; Awaji, A.; Tanaka, T.; Yamada, Y.; Bohland, J.; Tedesco, S.; Dal'Zotto, B.; Bruenger, W.; Torkler, M.; Fallmann, W.; Loeschner, H.; Kaesmaier, R.; Nealey, P. M.; Pawloski, A. R. *J. Vac. Sci. Technol., B* **1999**, 17, 3356–3361.

(9) Szmanda, C. R.; Kavanagh, R. J.; Bohland, J. R.; Cameron, J. F.; Trefonas, P., III; Blacksmith, R. F. *Proc. SPIE-Int. Soc. Opt. Eng.* **1999**, 3678, 857–866.

(10) Dill, F. H.; Hornberger, W. P.; Hauge, P. S.; Shaw, J. M. *IEEE Trans. Electron Devices* **1975**, ED22, 445–52.

(11) MacDonald, S. A.; Hinsberg, W. D.; Wendt, H. R.; Clecak, N. J.; Willson, C. G.; Snyder, C. D. *Chem. Mater.* **1993**, 5, 348–356.

(12) MacDonald, S. A.; Clecak, N. J.; Wendt, H. R.; Willson, C. G.; Snyder, C. D.; Knors, C. J.; Deyoe, N. B.; Maltabes, J. G.; Morrow, J. R.; McGuire, A. E.; Holmes, S. J. *Proc. SPIE-Int. Soc. Opt. Eng.* **1991**, 1466, 2–12.

increase in the induction time during development brought about by the base quencher may enhance resist pattern contrast. However, the presence of incomplete neutralization and dissolution promotion by the base will degrade pattern contrast. We believe the concepts elucidated in this work will be helpful for designing new photoresist systems and optimizing photoresist formulations by tailoring the composition of the base quencher for contrast enhancement.

## Experimental Section

**A. Materials.** The PTBOCST polymer, composed of poly-(*p*-hydroxystyrene) partially blocked with *tert*-butoxycarbonyl (tBOC) protecting groups, was obtained from Shipley Company. The photoacid generators, norbornene dicarboximide triflate (ND-Tf) and triphenylsulfonium triflate (TPS-Tf), were also obtained from Shipley Co. The base quenchers 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-piperidineethanol (1PE), and *N*-methyl pyrrolidinone (NMP) were purchased from Aldrich Chemical Co. and used as received. A 1.0 M solution of tetrabutylammonium hydroxide (TBAH) in methanol was also purchased from Aldrich. Photoresist solutions were formulated by weight from stock solutions of individual components dissolved in propylene glycol monomethyl ether acetate (PGMEA), with the exception of TPS-Tf that was in a solution of 2-heptanone. The concentration of PAG was 70  $\mu\text{mol}$  of PAG/g of solids ( $\pm 0.5$   $\mu\text{mol}$ /g) for each resist solution. For both PAGs a series of resist solutions was formulated for each of the four base quenchers. For every series the concentration of base ranged from 0 to 25% of the initial PAG concentration (0 to 0.25 base to PAG molar ratio). The solids content was controlled to 14 wt % by addition of PGMEA to the solutions.

**B. Sample Preparation and Processing.** Four-inch silicon wafers were primed with hexamethyldisilazane (HMDS) in a vacuum oven (Yield Engineering Systems) before resist application. Photoresist films for infrared (FTIR) analysis were coated on 4-in., high-resistivity (undoped) silicon wafers without HMDS priming. Resist films were spin-cast from solution on a resist spinner (Solitec) and baked on a hotplate (Silicon Valley Group 8600 track) at 115 °C for 60 s. Film thickness was measured using a Nanospec AFT 215 (Nanometrics) microscope or a Model F20 thin film measurement system (Filmetrics). The initial thickness of the resist films was  $590 \pm 8$  and  $665 \pm 23$  nm for the ND-Tf and TPS-Tf resist series, respectively.

X-ray exposures were performed using the Center for Nanotechnology's ES-1 beamline on the Aladdin electron storage ring of the Synchrotron Radiation Center at the University of Wisconsin. The X-ray radiation through the beamline and 75- $\mu\text{m}$  beryllium filter was calculated to have an average energy of 2516 eV using the TRANSMIT software application written by the Center for Nanotechnology.<sup>13</sup> All exposures were performed in a vacuum at <30 mTorr of nitrogen and without a mask (open frame). Exposure times were automatically corrected for attenuation of the beam current in the ring and converted to exposure dose values ( $\text{mJ}/\text{cm}^2$ ) using flux constants determined by calorimetry. After exposure, resist wafers were removed from the vacuum of the exposure chamber and baked on a hotplate (Silicon Valley Group 8600 track) at 100 °C for 90 s. The delay between the time of exposure and the postexposure bake was minimized to <7 min. Samples were developed with LDD26W developer (Shipley Co., 0.26 N aqueous tetramethylammonium hydroxide). The sensitivity of each resist formulation was taken as the exposure dose required for complete development of the resist film (dose to clear) after a 20-s development.

**C. Dissolution Rates of Exposed Photoresist Films.** Dissolution rates of exposed resist films were measured using a Development Rate Monitor 5900 (Perkin-Elmer) during

immersion in LDD26W developer solution. Measurements were performed using resist formulations containing a 10% loading of base (0.10 ratio base to PAG) and without base. Samples were prepared by exposing 2–9 regions across the axis of a wafer to allow simultaneous measurements for multiple exposed regions on a single wafer. The DREAMS software was used to calculate resist thickness as a function of development time. The dissolution rate was taken by a linear fit to the data at half-thickness. The induction time was measured as the duration of the initial slow dissolution period preceding development of the bulk of the resist film.

**D. Infrared Spectra for Exposed Resist Films.** Infrared reflectance spectra were measured for exposed and unexposed resist films formulated with and without base quenchers. For formulations containing base, the concentration of base was 7  $\mu\text{mol}$ /g (0.10 ratio of base to the initial PAG concentration). Identical processing conditions were followed for each resist. Resist films were exposed to X-rays with incremental increase in expose dose across 25 zones. Samples were baked but not developed after exposure. Infrared reflectance spectra were recorded for each of the 25 exposed regions from 650 to 4000  $\text{cm}^{-1}$  using the FilmExpert FTIR reflectometry workstation (On-Line Technologies) with a background reference to bare, undoped silicon. Spectra were collected at a resolution of 16  $\text{cm}^{-1}$  and averaged over 128 scans. After acquisition, reflectance spectra were analyzed using the FilmExpert software to calculate the dielectric function (absorbance) of the resist film.

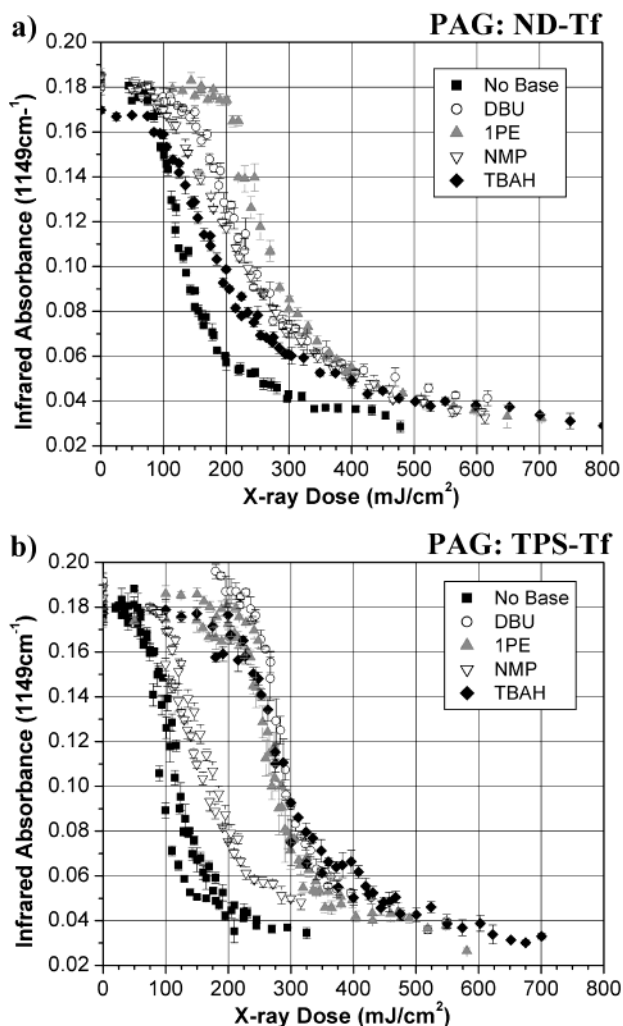
## Results and Discussion

**A. Neutralization of Photogenerated Acid by Base Quencher.** The infrared absorbance of resist formulations without base quencher and containing the base quenchers DBU, 1PE, NMP, and TBAH was measured as a function of X-ray exposure dose for systems containing the PAGs ND-Tf and TPS-Tf in PTBOCST. The absorbance at 1149  $\text{cm}^{-1}$  (C–O–C stretching of the *tert*-butyl ester) is proportional to the concentration of blocking groups remaining attached to the polymer and provides means for following the deprotection reaction. The decrease in absorbance is proportional to the extent of deprotection. Figure 2 shows the measured infrared absorbance at 1149  $\text{cm}^{-1}$  for each exposed region. Error bars represent the standard deviation of three measurements taken in each exposure zone. Compared to the resist without a base quencher, all of the systems containing base displayed an increase in the exposure dose required to achieve a given extent of deprotection. The increase in exposure dose is explained by neutralization of photogenerated acid by the base. As base neutralizes photoacid, the concentration of photoacid available to deprotect the resist (the free acid concentration) is reduced. Additional exposure is required to generate enough acid to reach the same extent of deprotection as a resist without base.

Despite the same concentration of base and identical processing conditions, the dependence of infrared absorbance on exposure dose was markedly different for several of the resists containing base. For example, in the ND-Tf system the exposure dose required to achieve a 10% reduction in the infrared absorbance was  $\approx 100$   $\text{mJ}/\text{cm}^2$  greater for a resist containing 1PE than for a resist containing TBAH. In the TPS-Tf system the formulations containing TBAH, DBU, and 1PE all exhibited nearly the same dependence of infrared absorbance on exposure dose, but the formulation containing NMP required significantly less exposure to drive deprotection. The data presented in Figure 2 indicate

(13) Cerrina, F.; Baszler, F.; Turner, S.; Khan, M. *Microelectron. Eng.* **1993**, *21*, 103–106.





**Figure 2.** Infrared absorbance for exposed resist films containing the PAGs (a) ND-Tf and (b) TPS-Tf, formulated with four base quenchers, DBU, 1PE, NMP, and TBAH. Error bars are the standard deviation of three measurements taken in each exposed region.

that these bases can act very different from each other in the resist film. Comparing results for the ND-Tf and TPS-Tf systems also suggests that the PAG influences the action of the base since the decrease in absorbance with dose in the ND-Tf system was different for all four bases, but in the TPS-Tf system three of the four bases exhibited the same behavior.

To investigate the acid–base chemistry between base quenchers and photoacid in resist films, the concentration of photoacid must be known for every exposure dose. The photoacid concentration was calculated at each exposure dose for which an infrared spectrum was taken using the photoresist  $C$  parameter determined by a standard addition experiment. The standard addition technique to quantify photoacid generation in chemically amplified photoresist has been described in detail elsewhere.<sup>6</sup> The  $C$  parameter represents the efficiency of the photochemical reaction and is proportional to the quantum yield of the photochemical decomposition of PAG to form photoacid. Once the  $C$  parameter is known for a particular resist system, the concentration of photogenerated acid within that resist may be calculated for any exposure dose. To determine the  $C$  parameters, 1PE was incorporated as the base quencher

into photoresist formulations containing the ND-Tf and TPS-Tf PAGs in PTBOCST. The use of 1PE as the base quencher for the standard addition technique was previously validated using the same PTBOCST polymer.<sup>6</sup> Values for the  $C$  parameter were determined as  $1.04 \times 10^{-3}$  and  $6.76 \times 10^{-4} \text{ cm}^2/\text{mJ}$  for the ND-Tf and TPS-Tf systems, respectively. The value of the  $C$  parameter was assumed to be independent of the type of base quencher. The average concentration of photo-generated acid,  $A_{\text{Gen}}$ , in the resist was calculated from

$$\langle A_{\text{Gen}} \rangle = \frac{P_0}{x_0} \int_0^{x_0} 1 - \exp\{-CD_0 e^{-\alpha x}\} dx \quad (1)$$

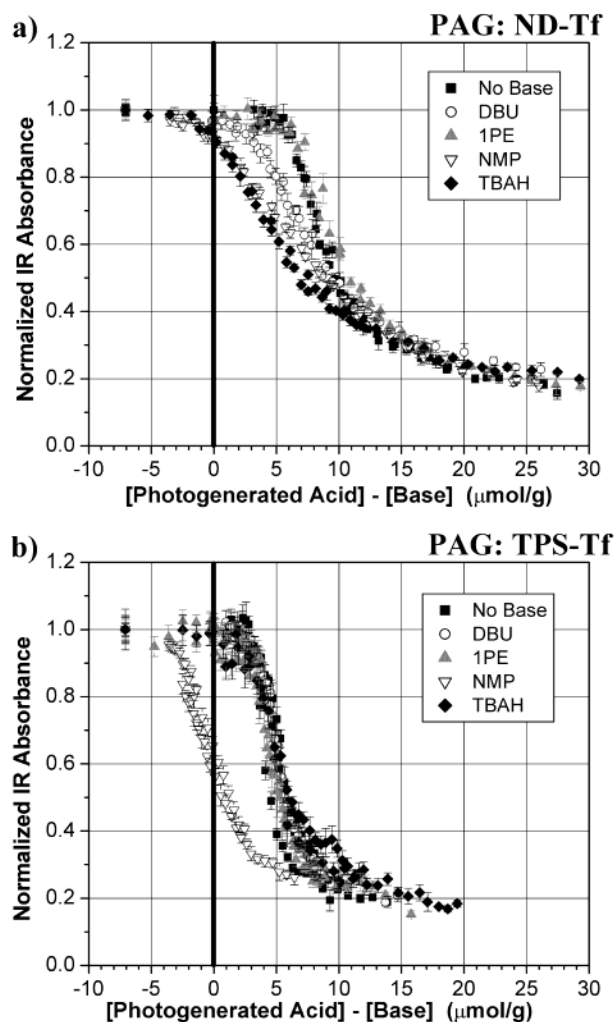
where  $P_0$  is the initial PAG concentration,  $x_0$  is the film thickness,  $D_0$  is the exposure dose incident to the resist, and  $\alpha$  is the absorption coefficient of the film. An absorption coefficient of  $0.022 \text{ } \mu\text{m}^{-1}$  for this resist system was calculated by atomic scattering cross sections.<sup>14</sup>

For systems containing base quenchers that neutralize photoacid, the concentration of photogenerated acid will be greater than the concentration of free photoacid available to catalyze deprotection. One requires knowledge of the kinetics and equilibrium of acid–base neutralization reactions to determine the exact concentration of photoacid that remains in the resist. The kinetics of acid–base neutralization reactions in photoresist have previously been investigated by Hinsberg et al. for a resist system consisting of the PAG di(*tert*-butylphenyl)iodonium perfluorobutanesulfonate (TBI–PFBS) in PTBOCST with TBAH as the base quencher.<sup>3</sup> On the basis of experimental and simulation results for this system, Hinsberg et al. proposed a proportional neutralization model to describe the neutralization of photoacid (perfluorobutanesulfonic acid) by TBAH. The proportional neutralization model states that the concentration of photogenerated acid formed upon exposure is immediately reduced (prior to the PEB) by an amount proportional to the concentration of base in the resist. The simplest implementation of this model is to assume that equilibrium strongly favors the production of neutral species, wherein base neutralizes a stoichiometric equivalence of acid. Additionally, the kinetics of the neutralization reaction are assumed to be sufficiently fast to reach equilibrium immediately after exposure, guaranteeing that acid–base reactions are completed prior to the PEB. The average free acid concentration,  $A_{\text{Free}}$ , in the resist film is then determined assuming stoichiometric neutralization by the relation

$$\langle A_{\text{Free}} \rangle = \langle A_{\text{Gen}} \rangle - B \quad (2)$$

where  $B$  is the concentration of base quencher added to the resist formulation. Deprotection of the resist during the PEB depends only on the concentration of free photoacid that remains after neutralization, and resists formulated with and without base quencher should reach identical extents of deprotection when the free acid concentration is the same. Using the assumption of fast, stoichiometric neutralization of photoacid by

(14) The absorption coefficient at 2516 eV was calculated based on the atomic composition of the polymer and the photoacid generator, assuming a density of  $1.15 \text{ g/cm}^3$ .



**Figure 3.** Normalized infrared absorbance at  $1149\text{ cm}^{-1}$  as a function of the free acid concentration in the resist for the PAGs (a) ND-Tf and (b) TPS-Tf. The coverage of blocking groups on the polymer is proportional to the infrared absorbance. The free acid concentration was calculated at each exposure dose that an infrared spectrum was measured using the resist  $C$  parameter determined by a standard addition technique and assuming stoichiometric neutralization of photoacid by base. Negative values represent base remaining in the film, and positive values indicate the free acid concentration within the film after the base has been completely consumed by neutralization.

base, the infrared absorbance data presented in Figure 2 were analyzed to reflect a dependence on the free acid concentration rather than exposure dose. Figure 3 displays the infrared absorbance (normalized to unexposed resist) as a function of the free acid concentration for both the ND-Tf and TPS-Tf resist systems without base and with each of the four base quenchers. Negative values of the free acid concentration represent the concentration of base that remains in the film.

The validity of the assumption of stoichiometric neutralization may be determined by comparing resist systems with and without base quencher. For stoichiometric neutralization of photoacid by base to occur, the resists formulated with and without base quencher should exhibit the same dependence of resist deprotection on the free acid concentration. Since the decrease in infrared absorbance is proportional to the extent of deprotection, the data presented in Figure 3 can be used

to determine agreement between systems with and without base. As seen in Figure 3, resist formulations containing 1PE and without a base quencher exhibited identical dependence of infrared absorbance on the calculated free acid concentration for both PAG systems. Additionally in the TPS-Tf system, formulations containing DBU and TBAH also showed the same behavior as the resist without base. The agreement of data between systems containing base (ND-Tf/1PE, TPS-Tf/1PE, TPS-Tf/DBU, and TPS-Tf/TBAH) and systems without base verified that the assumption of stoichiometric neutralization was valid to describe acid–base neutralization in these resists at the process conditions used.

If the equilibrium of the neutralization reaction does not strongly favor the formation of neutral products or if the kinetics of acid–base neutralization are slow, then it is possible that photoacid and base will simultaneously exist in the exposed regions of the resist film. For this case, base will not neutralize a stoichiometric concentration of photoacid. We have termed this case incomplete neutralization to describe the fact that all of the base quencher added to the resist has not been consumed before the concentration of free photoacid begins to increase in the resist. The actual concentration of photoacid available to catalyze deprotection will be greater than is expected for the case of stoichiometric acid–base neutralization. In effect, the deprotection of the resist during the PEB would appear to occur at lower values of the calculated free acid concentration than a resist without base.

As shown by the data presented in Figure 3, the ND-Tf/NMP, ND-Tf/DBU, ND-Tf/TBAH, and TPS-Tf/NMP resist systems did not demonstrate the same dependence on the decrease in infrared absorbance with the calculated free acid concentration (which assumed stoichiometric neutralization) as the counterpart formulations without base. The lack of agreement between systems with and without base indicated that the assumption of stoichiometric neutralization of photoacid by the base did not properly describe the acid–base chemistry of these resists. For these systems containing base, deprotection of the resist (decrease in infrared absorbance) appeared to occur at much lower free acid concentrations than for resists without base. These results suggest that the concentration of free photoacid in the resist was greater than predicted by stoichiometric neutralization, implying incomplete neutralization of the base quencher.

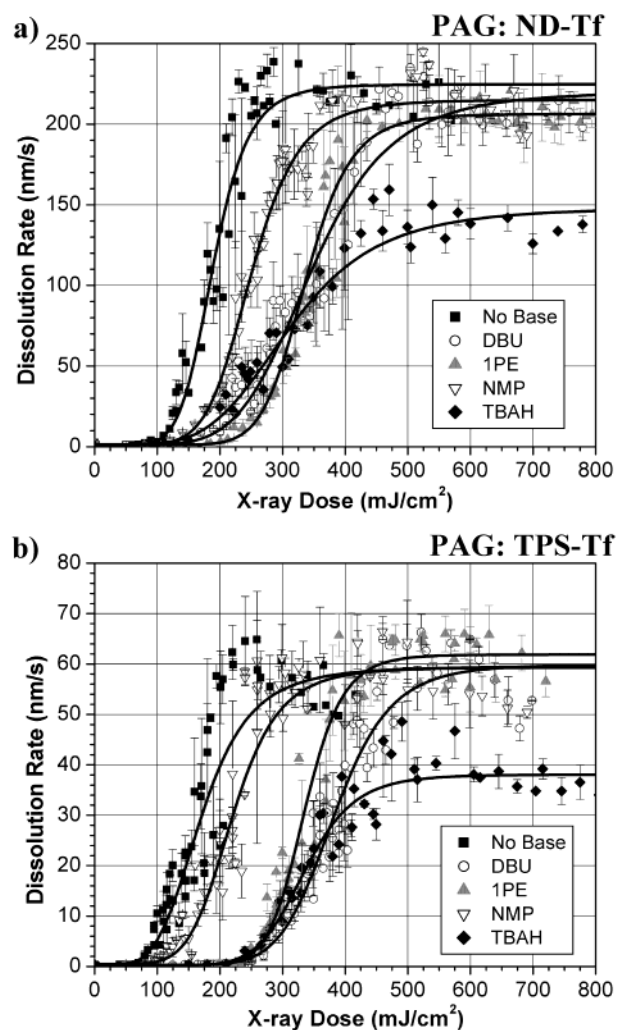
It is not clear from these experiments if the mechanism resulting in incomplete neutralization was due to acid–base equilibrium that did not strongly favor the products, slow reaction kinetics, diffusion limitations that constrained acid and base molecules from finding each other within the matrix, or a breakup of the acid–base complex during the postexposure bake. Interestingly, the composition of the PAG appeared to play a significant role in this effect. In the ND-Tf resist system the bases DBU and TBAH exhibited signs of incomplete neutralization, but in the TPS-Tf formulation these bases appeared to neutralize photoacid in stoichiometric concentrations. Since the polymer and type of photoacid (triflic acid) were the same for both PAG systems, the difference in the behavior of DBU and TBAH in these

resists was most likely related to the composition of the PAG and not the polymer or photoacid. Additional experiments will be required to characterize this effect of the PAG; however, these experiments suggest that by some process the PAG alters the physical or chemical properties of the resist film that influences the acid–base neutralization process.

**B. Base Strength of DBU, 1PE, TBAH, and NMP Base Quenchers.** The base strength of TBAH, DBU, 1PE, and NMP base quenchers was explored to determine if the relative strength of the quenchers was related to the process of incomplete neutralization of photoacid by base quencher. The base strength of base quenchers is extremely difficult to quantify in resist films. Data for the strength of organic bases in non-aqueous systems is limited, especially for mixtures in thin polymer films. To qualitatively compare the relative strength of the TBAH, DBU, 1PE, and NMP base quenchers in a common solvent, the  $pK_a$  of the conjugate acids for these bases were calculated in water. The predicted values of  $pK_a$  were obtained using the ACD/I-lab web service (Advanced Chemistry Development, Inc.). For the conjugate acids of TBAH, DBU, 1PE, and NMP the calculated  $pK_a$  values were  $15.7 \pm 0.1$ ,  $12.8 \pm 0.2$ ,  $9.0 \pm 0.2$ , and  $-0.14 \pm 0.2$ , respectively. The  $pK_a$  of trifluoromethansulfonic (triflic) acid, the photoacid generated by both PAGs, was calculated to be  $-6.85 \pm 0.15$  in water. The large difference in base strength between NMP, an amide, and the amines DBU and 1PE was expected from resonance stabilization of the amide.

A comparison of these  $pK_a$  values, albeit in aqueous solution rather than in a resist, suggests that all four base quenchers are indeed stronger bases than the conjugate base of triflic acid. On the basis of the large differences in  $pK_a$  values, a mixture of triflic acid with the bases TBAH, DBU, or 1PE would result in the equilibrium of the system favoring the formation of the reaction products (conjugate base of triflic acid and conjugate acids of the base quenchers). The difference in  $pK_a$  between triflic acid and TBAH, DBU, and 1PE bases is large enough to expect the reaction to occur essentially to completion, resulting in stoichiometric neutralization for an equal molar mixture of acid and base. However, for the case of NMP the formation of its conjugate acid is extremely unfavorable, and based on its low  $pK_a$  the fraction of associated base is extremely small. Therefore, the reaction of triflic acid with an equal concentration of NMP in water would produce an acidic solution and would not result in the stoichiometric neutralization of triflic acid.

Interestingly, NMP has been identified as an airborne contaminant and poison to chemically amplified resist processing, presumably due to the neutralization of photogenerated acid.<sup>11,12</sup> As shown in the previous section, ND-Tf and TPS-Tf resist formulations containing NMP did appear to neutralize some photogenerated acid but not in stoichiometric proportions. This behavior may be explained in part by the extremely weak base strength of NMP. However, ND-Tf/TBAH and ND-Tf/DBU systems also demonstrated incomplete neutralization, despite predictions from  $pK_a$  values that these bases should neutralize a stoichiometric concentration of photoacid. Despite extremely large differences in  $pK_a$  values, both ND-Tf/NMP and ND-Tf/TBAH resists



**Figure 4.** Dissolution rate of exposed resist films containing the PAGs (a) ND-Tf, and (b) TPS-Tf, formulated with the four base quenchers DBU, 1PE, NMP, and TBAH. Error bars are the standard deviation of the measurement. Solid lines are a fit of the data using eq 3.

exhibited nearly the same degree of incomplete neutralization. The calculated  $pK_a$  values in aqueous solution did not appear to even qualitatively predict the behavior of the base in photoresist with respect to acid–base neutralization. Furthermore, the calculated base strength cannot explain why DBU and TBAH exhibited stoichiometric neutralization in the TPS-Tf system but not in the ND-Tf system. The actual base strength of the quenchers may be very different in the resist film than in water, or the observation of incomplete acid–base neutralization (Figure 3) could be caused by another process.

**C. Resist Dissolution Dependence on Polymer Deprotection.** In previous work, we verified that the addition of 1PE to a ND-Tf/PTBOCST resist system did not alter the dependence of the dissolution rate on the extent of deprotection.<sup>6</sup> We have repeated an identical analysis for the resist systems in this work. The thickness of exposed resist films during development was recorded as a function of development time using a dissolution rate monitor. The dissolution rate was determined by a linear fit to the data at half remaining thickness. Figure 4 displays the dissolution rate dependence on exposure dose for the ND-Tf and TPS-Tf



systems. Error bars represent the standard deviation of the measurement. Each set of data was fit to the equation

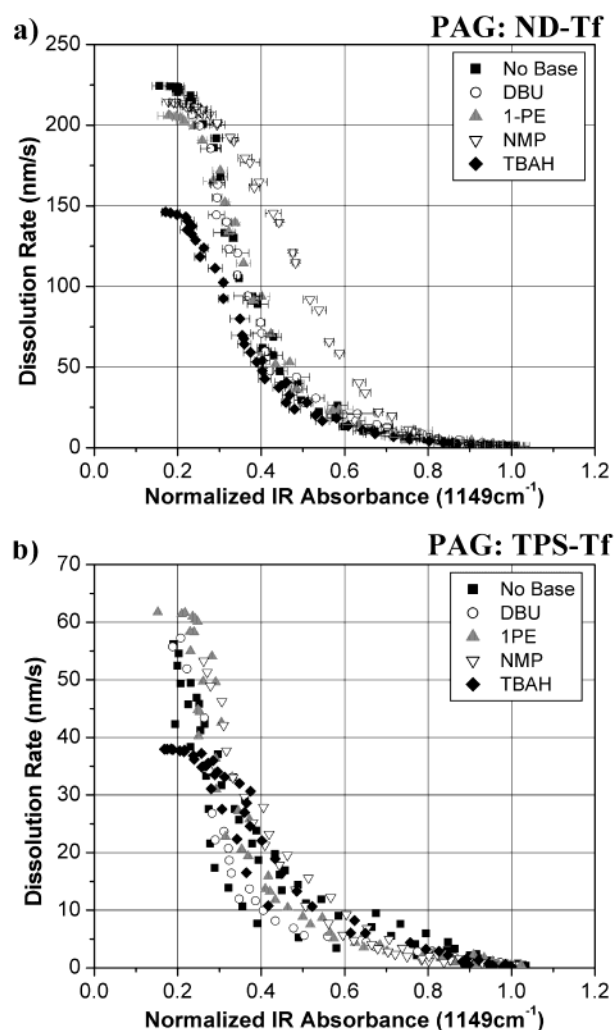
$$y = \frac{A_1 - A_2}{1 + (x/x_0)^p} + A_2 \quad (3)$$

where  $A_1$  and  $A_2$  represent the minimum and maximum dissolution rates and  $x_0$  and  $p$  are fitting parameters. Equation 3 does not represent a physical interpretation of resist dissolution and was only used to represent the form of the data.

The maximum dissolution rate of resists containing ND-Tf was much larger than for the TPS-Tf resists (approximately 215 vs 60 nm/s). Similarly, the minimum dissolution rate (unexposed resist) of the ND-Tf formulation was also larger than that for the TPS-Tf formulation (approximately 2.0 vs 0.3 nm/s). This showed that the TPS-Tf PAG was a more powerful dissolution inhibitor than the ND-Tf PAG; that is, the dissolution of the resist was slowed by the presence of the PAG in the resist formulation. The ratio of the maximum to the minimum dissolution rates defines the dissolution contrast of a resist. Ratios of 107 and 198 were calculated for the ND-Tf and TPS-Tf systems, respectively. The larger dissolution contrast for the TPS-Tf PAG suggests that greater image contrast can be achieved during patterning of this resist system. Additionally, TBAH was found to exhibit dissolution inhibition behavior. As shown in Figure 4, resist formulations containing TBAH exhibited a large decrease in the maximum dissolution rate for both photoacid generator systems. None of the other bases studied expressed this effect. The minimum dissolution rates of resists containing TBAH were not affected, indicating that the dissolution contrast of these resists was degraded by the addition of TBAH.

To demonstrate the dependence of the dissolution rate on deprotection, data for the dissolution rate as a function of exposure dose from Figure 4 was combined with the measurements of the infrared absorbance as a function of exposure dose shown in Figure 2. At every exposure dose that an infrared spectrum was taken, the dissolution rate was calculated using the parameters fit to eq 3. As shown in Figure 5, the dissolution rate is plotted as a function of the normalized infrared absorbance for the ND-Tf and TPS-Tf systems. The data include resist formulated without base and with the four bases DBU, 1PE, NMP, and TBAH. Data plotted in this manner are independent of the acid concentration and PEB conditions used to reach a given extent of deprotection since infrared absorbance directly measures the relative number of blocking groups on the polymer.

Figure 5 should represent a master curve of resist dissolution to the extent of deprotection as long as the addition of base did not alter the development of the resist as a dissolution inhibitor or promoter. Indeed, the dependence of the resist dissolution rate on the extent of deprotection was the same for the resists containing DBU and 1PE in the ND-Tf system. These formulations exhibited the same behavior as the resist formulated without base. The behaviors of formulations containing TBAH and NMP differed from the behavior of resist without base. As discussed above, TBAH reduced the maximum dissolution rate of the resist formulation. In

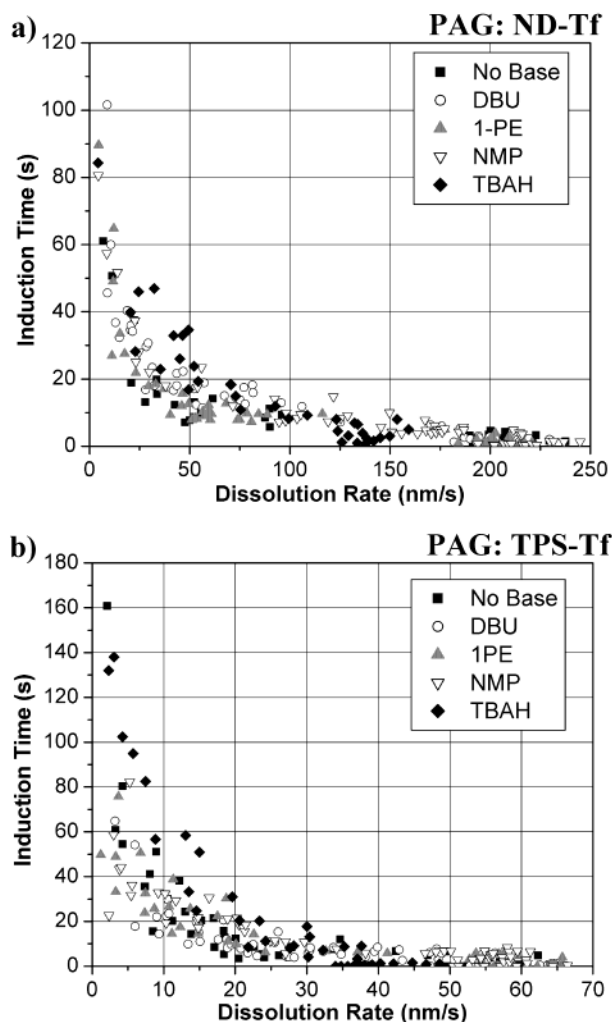


**Figure 5.** Dependence of the resist dissolution rate on the normalized infrared absorbance at  $1149\text{ cm}^{-1}$  for resists formulated with the PAGs (a) ND-Tf and (b) TPS-Tf containing the four base quenchers DBU, 1PE, NMP, and TBAH. Infrared absorbance is proportional to the number of protecting groups on the polymer. Data plotted in this manner are independent of the photoacid concentration or PEB conditions used to reach a given extent of deprotection.

addition to this effect, TBAH slightly decreased the dissolution rate compared to resist without base in the ND-Tf system below a value of 0.4 in the normalized infrared absorbance (high extent of deprotection). Above a value of 0.4 (low extent of deprotection), the behavior of the resist containing TBAH and no base quencher was the same. The dissolution rate for exposed resist films containing NMP as the base displayed a very large increase over resist without base quencher for nearly all levels of deprotection. This revealed that NMP promotes dissolution of the resist. The effect of the bases in the TPS-Tf resist system was much less clear due to scatter in the data. Nonetheless, the composition of the base even at concentrations as small as  $7\text{ }\mu\text{mol/g}$  within the resist has been shown by these experiments to affect resist dissolution by either dissolution inhibition or dissolution promotion processes.

#### D. Induction Effects during Resist Dissolution.

The dissolution of photoresist is a nonlinear process such that the initial dissolution rate of the resist during an induction period may be much slower than the



**Figure 6.** Induction time during resist dissolution as a function of the dissolution rate for resists containing the PAGs (a) ND-Tf and (b) TPS-Tf, with the four base quenchers, DBU, 1PE, NMP, and TBAH. Error bars have been omitted for clarity. Error in these measurements is large, as evident by the large degree of scatter in the data.

dissolution rate through the bulk of the film.<sup>15,16</sup> The dissolution rate measured by a dissolution rate monitor at half remaining thickness is therefore not necessarily equal to the average dissolution rate of the film as could be calculated by dividing the dissolved thickness by the development time. The duration of the induction period during dissolution was not constant and decreased with increasing exposure dose. The induction time, taken as the midpoint of the duration between the initial slow dissolution and the bulk dissolution of the resist film, was measured for the resist formulations in the previous section from the data collected by the development rate monitor. In Figure 6 the induction time is plotted as a function of the dissolution rate of the film at half thickness for the ND-Tf and TPS-Tf systems. The scatter in the data was large; however, in the ND-Tf resist system the induction time as a function of the dissolution rate was greater for resists formulated with

TBAH, NMP, and DBU bases as compared to resist without added base. The induction time as a function of the resist dissolution rate for the TPS-Tf system appeared to be increased by TBAH and unaffected by the other bases. The addition of 1PE maintained the same dependence of the induction time on the dissolution rate as the resist without base quencher for both the ND-Tf and TPS-Tf systems. Additionally, the increase in the induction time brought about by the addition of base was more significant at slow dissolution rates than for fast dissolution rates.

The effects of dissolution induction are important because photoresist processing uses a constant development time. A long induction time during dissolution reduces the remaining amount of time to dissolve the majority of the resist film. A resist with a long induction time will require a greater dissolution rate to develop the same resist thickness as a formulation with a small induction time. To increase the dissolution rate, a greater number of protecting groups must be removed from the polymer, requiring a larger concentration of photoacid and increasing of the exposure dose.

The concentration of base in each resist formulation was 7  $\mu\text{mol/g}$ . This small amount of base was able to alter the induction time of dissolution for some resist formulations and may provide an added benefit to lithographic patterning. Ideally, a resist would have a large induction time when unexposed and absolutely no induction once the dissolution rate of the resist reaches a value sufficient to produce good contrast between exposed and unexposed resist. The contrast of the resist pattern would then be slightly improved by reducing the thickness loss in the unexposed regions. This enhancement may be even more beneficial for exposures with phase-shifting masks, where extremely high resist contrast is required to compensate for the threshold between phase-shifted intensities.<sup>17</sup>

**E. Effects of Base Quenchers on Photoresist Sensitivity.** Figure 7 displays the dose to clear as a function of the base concentration within the resist for the four quenchers. The similar dose to clear values for the ND-Tf and TPS-Tf resists without added base were coincidence. Since the base neutralizes photoacid, the dose to clear increased as expected for an increase in the base concentration. However, the relative increase in the dose to clear depended on the composition of the base.

The sensitivity of a photoresist is generally described by its dose to clear for a given thickness and processing conditions. Resists that require lower exposure doses are considered to be more sensitive resists. It is often difficult to understand what effect the individual components of a resist will have on its sensitivity since it is a convolution of many effects, from the efficiency of photoacid generation to the resist dissolution behavior. Nonetheless, resist sensitivity is an extremely important parameter for the design of chemically amplified resists to maximize the throughput of exposure tools.

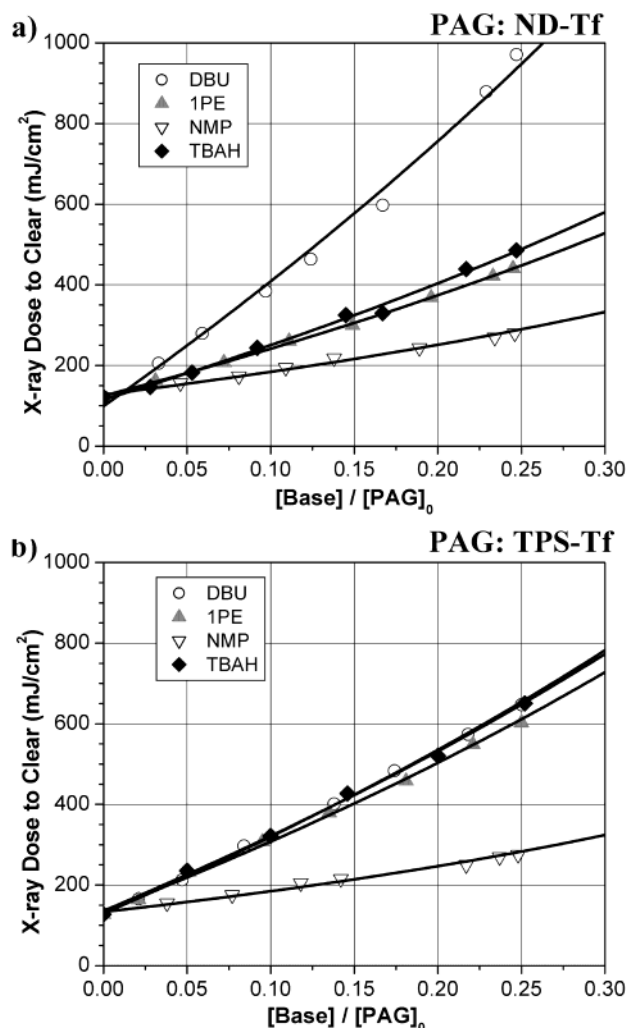
The effect of the addition of base on the sensitivity of these resists can be explained by the experiments performed above. In the previous sections, only the base 1PE was found to maintain the same deprotection and

(15) Burns, S. D.; Gardiner, A. B.; Krukonis, V. J.; Wetmore, P. M.; Lutkenhaus, J.; Schmid, G. M.; Flanagan, L. W.; Willson, C. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **2001**, 4345, 37–49.

(16) Flanagan, L. W.; Singh, V. K.; Willson, C. G. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, 37, 2103–2113.

(17) Yang, L.; Taylor, J. W. *J. Vac. Sci. Technol., B* **2001**, 19, 129–135.





**Figure 7.** Dose to clear as a function of base concentration for resists formulated with (a) ND-Tf and (b) TPS-Tf and the four base quenchers DBU, 1PE, NMP, and TBAH. The measurement error for the determination of the dose to clear is typically within  $\pm 5$  mJ/cm<sup>2</sup>.

dissolution behavior as a system without base. Also, the neutralization of photoacid by 1PE appeared to be fast and to go to completion before the PEB. The role of the 1PE base in these resist systems was therefore considered to act only to neutralize a stoichiometric amount of photoacid. The increase in the dose to clear with increasing base concentration as seen in Figure 7 for 1PE formulations was then only an effect of photoacid neutralization. Since the 1PE base acts only to neutralize photogenerated acid, the 1PE resist series was used as a basis of comparison for evaluating the effects of the NMP, DBU, and TBAH base quenchers on resist sensitivity.

The dose to clear values for the ND-Tf/NMP and TPS-Tf/NMP resists were much lower than those of their respective systems containing 1PE. As shown in Figure 3, the resists formulated with NMP were found to exhibit deprotection of the polymer before the base was completely neutralized in both PAG systems. Additionally, resists containing NMP produced a greater dissolution rate at lower values of deprotection than for the system without base, as seen in Figure 5. Both of these effects reduced the concentration of photogenerated acid that must be created during exposure to drive

sufficient deprotection and render development. The induction time during dissolution of the ND-Tf resist was increased by the addition of NMP as shown in Figure 6 and could increase the exposure dose needed to develop the resist, but this effect was small compared to the influence of NMP on the acid–base neutralization and dissolution promotion processes.

The large increase in the dose to clear for resists containing DBU as compared to 1PE was due to increased induction time. In Figure 6, the induction time for the resist formulated with DBU with the ND-Tf PAG was longer than that for the resist without added base. Since the development time was constant, an increased induction time demanded an increase in the dissolution rate of the resist to clear the film during development. To increase the dissolution rate, a larger exposure dose was required to generate additional photoacid. Interestingly, the ND-Tf resist containing DBU also permitted some deprotection of the polymer before complete neutralization of the base, as shown in Figure 3. Although this should decrease the dose to clear, the increased induction time appeared to have a greater effect. In the TPS-Tf resist system, the incorporation of DBU into the resist formulation did not appear to increase the induction time during development, but the dose to clear as a function of the added base concentration was slightly greater for the resist containing DBU as compared to the 1PE resist series. The small increase in the dose to clear may be due to an increased induction time that cannot be resolved within the uncertainty of our measurements.

The resist system containing TBAH as the base revealed a slight increase in the dose to clear as compared to the system containing 1PE for both PAGs. The effects of dissolution inhibition by TBAH at high extents of deprotection (low values of infrared absorbance) shown in Figure 5 did not appear to influence the measurement of the dose to clear since the extent of deprotection for these process conditions was relatively low.<sup>18</sup> The induction time during dissolution for the TBAH resist formulated with both PAGs was larger than that for the systems containing 1PE as seen in Figure 6. The longer induction time for the resist containing TBAH in the TPS-Tf system increased the dose to clear for the TBAH series as compared to the 1PE series. Similarly in the ND-Tf system, the induction time for resists containing TBAH was longer than that for resists containing 1PE or DBU. One may expect the dose to clear for the ND-Tf/TBAH system to be greater than that for the ND-Tf/DBU system since TBAH produced a greater increase in the induction time than DBU. However, a greater extent of deprotection occurred at small concentrations of photogenerated acid for the ND-Tf/TBAH resist than for the ND-Tf/DBU resist as shown in Figure 3. This counteracts the increase in dose to clear, which would be caused by an increased dissolution induction time. The end result of

(18) For example, at a 10% loading of TBAH in the ND-Tf resist system the dose to clear was approximately 250 mJ/cm<sup>2</sup>. For this dose the infrared absorbance of the resist was approximately 0.07 as seen by Figure 2, making the normalized infrared absorbance of the TBAH resist about 0.4. For values above 0.4 the normalized infrared absorbance of the resist containing TBAH lies on the master curve displayed in Figure 5 and appears to have the same behavior as the system containing 1PE or no base quencher.

**Table 1. Summary of the Effects Observed for 1PE, DBU, TBAH, and NMP Base Quenchers in Resist Formulations Consisting of ND-Tf and TPS-Tf Photoacid Generators in PTBOCST<sup>a</sup>**

| PAG: ND-Tf base | incomplete neutralization | dissolution inhibition | dissolution promotion | induction time | resist sensitivity compared to 1PE |
|-----------------|---------------------------|------------------------|-----------------------|----------------|------------------------------------|
| 1PE             | no effect                 | no effect              | no effect             | no effect      |                                    |
| DBU             | ✓                         | no effect              | no effect             | +              | –                                  |
| TBAH            | ✓                         | ✓                      | no effect             | +              | –                                  |
| NMP             | ✓                         | no effect              | ✓                     | +              | +                                  |

| PAG: TPS-Tf base | incomplete neutralization | dissolution inhibition | dissolution promotion | induction time | resist sensitivity compared to 1PE |
|------------------|---------------------------|------------------------|-----------------------|----------------|------------------------------------|
| 1PE              | no effect                 | no effect              | no effect             | no effect      |                                    |
| DBU              | no effect                 | no effect              | no effect             | no effect      | –                                  |
| TBAH             | no effect                 | ✓                      | no effect             | +              | –                                  |
| NMP              | ✓                         | no effect              | ✓                     | no effect      | +                                  |

<sup>a</sup> ✓: effect is present; + increase; – decrease.

these competing processes only raised the dose to clear by a small amount compared to that of the 1PE series.

### Conclusions

This work illustrated that the role of base quenchers inside films of chemically amplified photoresist can be more complex than simple acid–base neutralization. The results suggest that even small concentrations of these components may lead to large variations in the physical or chemical properties of the material. Furthermore, the effect of the base on the resist can change with the composition of the PAG. Table 1 summarizes the effects that have been observed for these four base quenchers in formulations consisting of the ND-Tf and TPS-Tf PAGs in PTBOCST. A comparison of the four base quenchers DBU, 1PE, NMP, and TBAH has indicated that only one of these bases, 1PE, maintained the same dissolution and deprotection qualities as resist without added base. NMP was found to promote dissolution of resist in aqueous base, while TBAH inhibited resist dissolution at high extents of deprotection. Resist formulations containing DBU and TBAH bases appeared to have a greater induction time during resist dissolution as compared to resists without added base. Incomplete neutralization of photoacid by DBU, NMP, and TBAH was observed in the ND-Tf system, but only the NMP formulation in the TPS-Tf system showed deprotection before complete neutralization of photoacid. These important results demonstrate that the base quencher performs a multifunctional role in chemically amplified resist.

The use of base quenchers as analytical reagents in resist films may be affected by the action of the base. For example, the standard addition technique requires that the base act only to neutralize a stoichiometric concentration of photoacid. Of the four bases studied in this work, only 1PE meets this criterion. Attempting to use DBU, NMP, or TBAH as the base with a PTBOCST polymer would lead to erroneous values for the *C* parameter since these bases can alter the dissolution

and deprotection of the resist beyond the stoichiometric neutralization of photogenerated acid. Additionally, there are important consequences for lithographic imaging by the selection of the base quencher. Dissolution promotion in the unexposed regions of a resist film would limit contrast between unexposed and exposed regions. The incorporation of NMP would therefore likely degrade resist contrast. Dissolution inhibition can often increase the contrast of patterned films by increasing the ratio of the maximum to minimum dissolution rate. TBAH does appear to inhibit dissolution by reducing the maximum dissolution rate; however, TBAH is not expected to improve resist contrast by inhibition for these systems since the minimum dissolution rate is not reduced significantly. A long induction time during resist dissolution can also enhance pattern contrast since resist development is performed at fixed times. Quenchers that increase the induction time, like DBU or TBAH, may improve contrast by reducing the resist thickness loss in the unexposed regions. Line width control can be enhanced using base quenchers but will likely lose effectiveness if the base does not completely neutralize the photoacid in a stoichiometric fashion.

**Acknowledgment.** The authors are grateful to David Medeiros, Charles Szmanda, and Frank Houlihan for their assistance and insightful discussions. Gratitude is also expressed to the Semiconductor Research Corporation for their funding through the Graduate Fellowship program. This work is based in part by a grant from the Semiconductor Research Corporation under Grant 98-LP-452. The Center for Nanotechnology, University of Wisconsin–Madison, is supported in part by DARPA/ONR Grant N00014-97-1-0460. The Synchrotron Radiation Center of the University of Wisconsin–Madison is supported by the National Science Foundation under Grant DMR-0084402.

CM0200947