Resolution limitations in chemically amplified photoresist systems[§]

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ABSTRACT

A variety of experimental evidence suggests that positive-tone chemically amplified photoresists have an intrinsic bias that might limit resolution during high-volume lithographic processing. If this is true, the implications for the semiconductor industry require careful consideration. The design concept of chemical amplification is based on generation of a chemically stable catalytic species in exposed regions of the photoresist film. The catalytic action of the photoproducts on the photoresist polymer causes a change in the dissolution rate in the irradiated regions of the film. Formation of a stable catalyst species is required for chemical amplification, but it has long been recognized that catalyst migration can produce a difference between the initial distribution of exposure energy and the final distribution of photoproducts. This difference, known as diffusion bias, depends on the photoresist chemistry and processing conditions. Diffusion bias is insensitive to exposure conditions, but it is possible to reduce catalyst migration through changes to resist formulation such as increasing the size of the catalyst molecule or processing conditions such as reducing the post exposure bake temperature. Another common approach to limiting diffusion bias is to incorporate base additives into the photoresist formulation to scavenge diffusing acid catalyst. All of these approaches to reducing catalyst migration generally reduce the catalytic efficiency of each photoproduct and therefore increase the total exposure dose required to pattern the film. Increases in required exposure dosage reduce the throughput of the exposure tools and can reduce the profitability of the manufacturing process. In this paper we present experimental results that are suggestive of an intrinsic photoresist bias. This diffusion bias sets a minimum resolution limit for chemically amplified resist systems that can be improved at the cost of reduced throughput and productivity.

Keywords: photolithography, chemically amplified photoresist, resolution limit

INTRODUCTION

Chemically amplified resists (CARs) are compatible with high-throughput manufacturing processes because of their high photosensitivity, which reduces the time required to expose a mask field. The design concept of chemical amplification is based on the generation of a chemically stable catalytic species in irradiated regions of the photoresist film.[1] The catalytic action of the photoproducts on the photoresist polymer during a post-exposure bake (PEB) step causes a change in the dissolution rate in the irradiated regions of the film. A single photo-generated catalyst molecule can facilitate hundreds of chemical reactions that alter the solubility of the exposed regions and thereby provide *chemical amplification* of the exposure dose. Formation of a stable catalyst species is essential for chemical amplification, but it has long been recognized that migration of this catalyst can limit the ultimate resolution of these systems.[1] Diffusion of catalyst from exposed to unexposed regions of the film results in a difference between the distribution of exposure energy and the final distribution of exposure photoproducts. This difference, known as *diffusion bias*, not only complicates feature dimension control, but also determines the best resolution that could be attained by an ideal exposure system with infinitesimal exposure linewidth.

The first successful photoresist based on chemical amplification consisted of poly(t-butoxycarbonyloxystyrene) (PTBOCST) with several weight percent of triphenylsulfonium hexafluoroantimonate, a photoacid generator (PAG).[2] Exposing this material to ultraviolet radiation produces a strong acid. At the elevated temperature of a subsequent PEB,

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the acid catalyzes the thermolytic deprotection of PTBOCST to poly(p-hydroxystyrene) (PHOST). (See Figure 1.) While this material can be imaged in either positive or negative tone with proper choice of developing solvent,[1] it is most commonly imaged in the positive tone through development in an aqueous base solution. The general imaging mechanism of the PTBOCST/PAG system – acid-catalyzed conversion of polymer from hydrophobic to hydrophilic – has been copied by every subsequent positive tone CAR used in manufacturing. This PTBOCST/PAG system has often served as a simplified model system for fundamental studies of more advanced positive tone CARs.

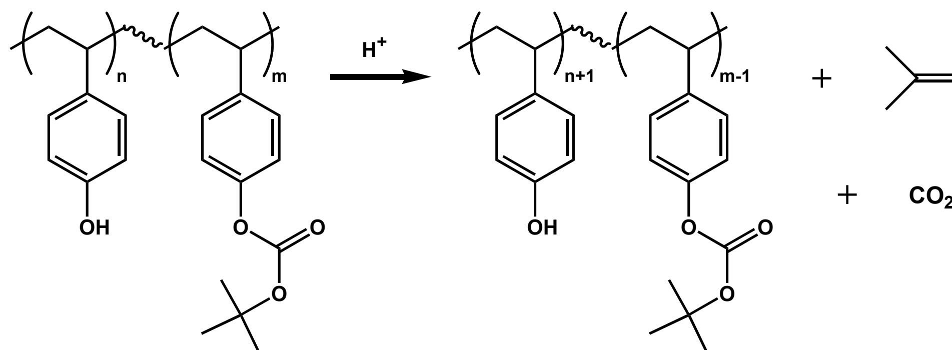

Figure 1. Acid-catalyzed thermolytic conversion of PTBOCST to PHOST.

INTRINSIC RESOLUTION LIMITS IN POSITIVE TONE CHEMICALLY AMPLIFIED RESISTS

For many years, improvements in lithographic resolution were achieved by formulating photoresists that could be imaged at shorter ultraviolet wavelengths. Illumination at shorter wavelengths facilitates reduced exposure linewidth, and photoresists were able to translate these improvements in exposure capability into improvements in resolution. However, diffusion bias is intrinsic to the photoresist chemistry and processing and can not be eliminated by improving the exposure process. One of the first studies to look for an intrinsic resolution limit in CARs was conducted by exposing a film of PTBOCST/PAG with a scanning transmission electron microscope (STEM) having a beam diameter approaching 0.6 nm at 50 kV.[3] The photoresist film was cast on a thin film of silicon nitride (~200 nm thick) to reduce the effects of exposure by backscattered electrons, and a pattern containing lines of varying width was exposed at various doses. When developed in the negative tone by a nonpolar solvent, the resist was reported to have a resolution of 18 nm (isolated line). However, these materials are traditionally imaged in the positive tone by an aqueous base solution. Exposure of the PTBOCST/PAG resist in a STEM and development in a polar developer produced isolated trenches as small as 40 nm. The difference between the exposure linewidth of approximately 0.6 nm and the developed linewidth of 40 nm suggests that the average diffusion length of active catalyst species is approximately 20 nm.

Another approach to probing the resolution of a resist material at the limit of infinitesimal exposure linewidth is through use of physically based, experimentally calibrated computer models. Through use of such a model, Hinsberg and coworkers have calculated line spread for Shipley UVIIHS,[#] an ESCAP family resist.[4] ESCAP materials[5] are mature among CARs, in that these photoresists have been extensively optimized and implemented in manufacturing processes (whereas the PTBOCST/PAG system, the original CAR, is no longer used in mass production). The calculated distribution of reaction products is much broader than the initial distribution of acid and can be fit with a truncated Lorentzian function with full width at half maximum (FWHM) of 51 nm. This value is suggestive of an average diffusion length for active catalyst species of approximately 25 nm.

[#] Certain commercial equipment and materials are identified in this article in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

While the references above report resolution studies for isolated features, real lithographic processes often require imaging dense features (*e.g.* equal line/space gratings) at high resolution. Interferometric lithography is well suited for producing such grating structures, and has been used for evaluating new photoresist materials. Hinsberg *et al.* have compiled data[4] from interferometric exposure of ESCAP CARs to examine the effect of reduced pitch on image quality. Exposure of ESCAP resists at 200 nm pitch (257 nm exposure)[6] and 90 nm pitch (257 nm immersion exposure)[6] demonstrate resolved dense features, but feature quality is severely degraded at 60 nm pitch (157 nm immersion exposure)[7] and 38 nm pitch (13 nm exposure)[8]. The maximum dense resolution that is demonstrated by these data (pitch = 90 nm) corresponds to an average diffusion length of less than 22 nm for active catalyst molecules.

MEASURING DIFFUSION BIAS

One method that has been used to analyze the transport properties of photogenerated acid within a photoresist film is to study the change in dimension of photoresist features with changes in duration of the PEB step.[9] Changes in feature dimension with PEB duration are directly affected by catalyst migration, but it is difficult to extract the contribution to bias that is purely the result of acid diffusion. The measured bias is a combination of contributions not only from acid diffusion, but also from gradients in exposure intensity and issues related to the development step. Our experimental approach is designed to isolate the contribution of acid diffusion to overall dimensional bias. The experiment is described in detail elsewhere,[10,11] but briefly explained, acid diffusion is studied using a bilayer film stack in which one film layer contains acid in a matrix of inert polymer and the other film is reactive towards acid, but is initially acid-free. When the bilayer film stack is baked, acid diffuses from the “acid source layer” into the “acid detector” layer. The acid diffusion length is determined by measuring the progress of the deprotection reaction in the reactive layer through reflectance-mode Fourier transform infrared (FTIR) spectroscopy. The initial bilayer studies yielded average diffusion lengths for active catalyst species in the range of (25 to 50) nm for a 90 s PEB.[10-12]

Neutron reflectometry (NR) has also been used to measure the diffusion length in bilayer samples.[13] This measurement is made possible through use of a model polymer that exhibits measurable neutron scattering contrast between the unreacted and reacted compositions. Contrast has been achieved by deuterium labeling of the acid-labile *t*-butyl protecting group present in PTBOCST, and is a result of the large difference in neutron scattering length between a proton (-3.74×10^{-13} cm) and a deuteron (6.67×10^{-13} cm). In the presence of acid at elevated temperature, the deuterated portion of this dPTBOCST polymer is thermolytically cleaved and the deuterated by-products desorb from the film. NR measurements of acid transport in a bilayer film stack indicate that the average diffusion length of active catalyst species is about 19 nm for a 90 s PEB at 100 °C.

When studying diffusion across an interface, as in the bilayer experiments described above, it is important that the layers are in good physical contact but without any interlayer mixing. This has been confirmed through SEM studies in which a chemical decoration technique enabled simultaneous visualization of the interface and the acid diffusion length.[10] NR measurements also indicate that the interface between layers is sharp, having interfacial widths in the range of (1 to 4) nm. The acid reaction diffusion pathway can be directly observed in single-layer photoresist films comprising a small concentration of acid in a matrix of dPTBOCST using small angle neutron scattering (SANS).[14] At these low concentrations of acid, each acid molecule is (on average) well separated from other acid molecules and the reacted volumes initially grow independently of one another. NR measurements have been interpreted by modeling the system with isolated spheres having a composition (*i.e.*, neutron scattering length density, NSLD) that varies with distance from the center of the sphere. The reaction-diffusion volumes in this study were modeled with a Gaussian distribution in NSLD having a characteristic radius of (11 ± 3) nm.

APPROACHES TO REDUCING DIFFUSION BIAS

Diffusion bias can be reduced by changes in both resist processing and formulation. From the processing side, perhaps the simplest method to reduce bias is to decrease the PEB time; shorter bake times reduce the time available for diffusion. Alternatively, reducing the PEB temperature can decrease diffusion rates. Changes in resist formulations, such as increasing the molecular size of the photogenerated acid, can reduce diffusion-induced bias. Increasing the loading of base additives also reduces diffusion bias by scavenging acid that diffuses from nominally exposed regions into

nominally unexposed regions. Unfortunately, all of these routes to reducing diffusion bias have a common drawback – they also reduce resist sensitivity. This unfortunate tradeoff is inherent to the very nature of chemically amplified photoresists: reducing acid diffusion means limiting the number of reactants to which an acid molecule can diffuse, which in turn limits the number of reactions that each photogenerated acid molecule can catalyze. To understand the limits of this tradeoff, we now turn to an investigation of the relationship between the mechanisms responsible for high sensitivity and the processes that limit resolution in positive-tone CARs.

Reducing diffusion bias through process variables

Bake processing can be tuned to control diffusion bias in several ways. One approach is to increase the temperature and/or duration of the post-apply bake (PAB) to promote annealing of the polymer-based film and thereby reduce the diffusivity of penetrants; this is the inspiration behind ESCAP-type resists.[5] Most commercial photoresists already have optimized PAB parameters designed to limit diffusion of atmospheric base contaminants while minimizing undesirable thermolytic decomposition of the polymer. Modification of PAB parameters to limit acid diffusion can not be performed independently from these other considerations, so further reduction in acid diffusion bias via optimization of PAB parameters will not be possible until these other processing restrictions are somehow relaxed. This might be possible, for example, by more stringent control of ambient base contaminants or reduced susceptibility to thermolytic decomposition.

Another approach to reducing diffusion bias is to reduce the duration of the PEB step, thus reducing the time available for diffusion and reaction to occur. At the onset of the PEB, there is an excess of reactive polymer and the reaction occurs at a rate that is a direct function of the processing temperature. As the reactive polymer becomes increasingly depleted, the reaction can only occur when acid diffuses to the remaining reactive regions. At this stage, the reaction is limited by acid transport and the overall rate is greatly reduced. In practice, PEB steps are typically allowed to progress well into the relatively slow, diffusion-limited regime to facilitate process control. Therefore, while it is possible in principle to minimize diffusion bias by implementing a short PEB, in practice the high initial rate of reaction would make it very difficult to attain an acceptable level of process repeatability.

Reducing the temperature of the PEB can reduce diffusion bias by reducing the diffusivity of the acid catalyst. The relationship between diffusivity and temperature is typically an Arrhenius exponential, and a relatively small decrease in bake temperature can cause a significant reduction in diffusion rate. The relationship between acid diffusion length, bake temperature, and bake duration has been studied in a series of FTIR bilayer experiments. The acid source layer contained 10 % by mass triphenylsulfonium perfluorobutanesulfonate in an inert matrix of poly(*p*-methoxystyrene), and the top detector layer was a 320 nm thick film of PTBOCST. Figure 2 presents diffusion distances measured at several different temperatures in the range of 75 °C to 110 °C over the course of a 10 min PEB. The results in Figure 2 demonstrate that it is possible to decrease acid diffusion distances by reducing PEB temperature. However, the rate of chemical reaction is also characterized by an Arrhenius expression, and reducing the bake temperature will also reduce the reaction rate. To achieve the same extent of reaction would then require a longer PEB (which would increase diffusion bias) or a higher initial concentration of acid (which would require a larger exposure dose). A reduction in PEB temperature could be tolerated if the overall rate of reaction were increased, but the rate of reaction is already designed to be very large. It is known that the acid-catalyzed thermolytic conversion of PTBOCST to PHOST is somewhat autocatalytic because the rate of reaction increases as the initial PTBOCST matrix is converted into PHOST. It might be possible to increase the autocatalytic nature of the reaction and thereby decrease the time required to achieve the desired extent of reaction in the highly exposed regions while decreasing the relative rate of reaction in regions receiving light exposure.

A more effective way to reduce diffusion bias is to design the photoresist such that the rate of acid diffusion at the processing temperature is reduced without reducing the rate of chemical reaction. For example, the acid-catalyzed thermolysis reaction occurs at room temperature in certain positive-tone CARs.[15] These systems do not require an elevated-temperature PEB, but effectively function via a room temperature PEB of indefinite duration. While these chemically amplified materials are notably different in the way that they are processed, the room-temperature PEB processing is actually an example of an approach to reducing diffusion bias by changing the chemical formulation of the resist.

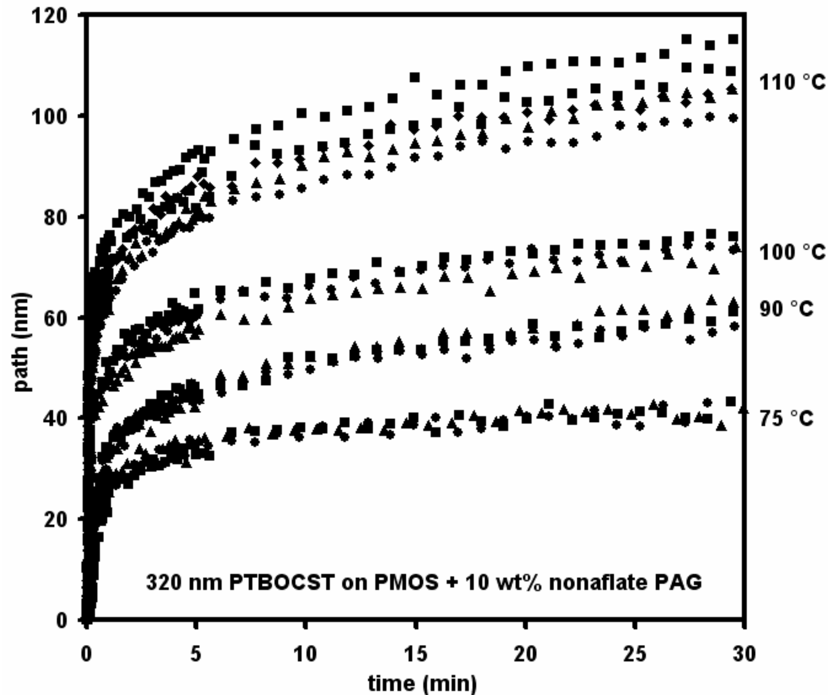

Figure 2. Bilayer diffusion distance at several temperatures

Reducing diffusion bias through resist formulation variables

A common resist formulation change used to control diffusion has been to vary the size of the conjugate base of the photoacid. The acidic proton does not exist alone; to maintain charge neutrality the proton is accompanied by a counter-ion. Shi[15] has analyzed the Coulombic interactions of the acidic proton/counter anion in photoresist materials and determined the acid and anion diffuse as a coordinated complex. This is supported by experimental observations that changes in the size of the acid counter-anion alter the measured diffusivity.[16-18] The earliest CAR formulations used hexafluoroantimonic acid partly because the large counter-anion was expected to limit diffusion. Non-metallic PAGs have been preferred over hexafluoroantimonate PAGs in recent years due to concerns about device contamination. State-of-the-art photoresists once used trifluoromethanesulfonate (triflate, $CF_3SO_3^-$) PAGs. Perfluorobutanesulfonate (nonaflate, $C_4F_9SO_3^-$) PAGs later became popular, followed by perfluorooctanesulfonate (PFOS, $C_8F_{17}SO_3$) PAGs. (PFOS PAGs have since lost favor due to environmental health and safety concerns.) The effect of increased penetrant size on diffusion rate is a well studied area of polymer membrane science. Figure 3 demonstrates the effect of acid counter anion size on measured diffusion distance. A bilayer experimental method was used with constant PAG molar loadings in the acid feeder layer at a PEB temperature of 90 °C. The tested PAGs were a triflate, a hexaflate ($C_3F_6HSO_3$), a nonaflate, an antimonate, and a polymeric PAG. The polymeric PAG[18] generates an acid with a conjugate base that is covalently linked to a polymer chain. In this case, the counter-anion is a polymer chain with low mobility, and any reaction that occurs in the adjacent PTBOCST layer results from separation of the acid from its counter-ion. This separation occurs even in the absence of diffusion, and can be considered the minimum amount of bias that is possible in a chemically amplified resist. A surprisingly large apparent diffusion distance of 25 nm was measured for a 3 min, 90 °C PEB using the polymeric PAG.

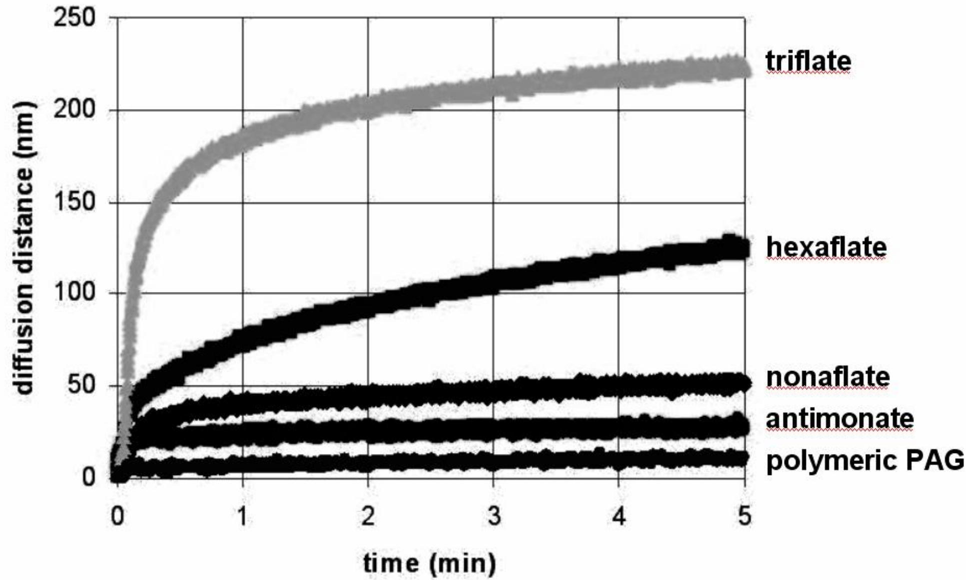

Figure 3. Bilayer diffusion distance for several acids of varying size

In a separate series of bilayer experiments, NR was used to monitor the reaction at the interface between a polymeric PAG film and a film composed of dPTBOCST similar to the experiment presented earlier, but the dPTBOCST layer was floated onto the PHOST layer rather than directly spin-coated[13]. The polymeric PAG used in this study consisted of a copolymer of *p*-methoxystyrene and a PAG species as shown in Figure 4; the synthesis of this material is reported elsewhere.[19] Upon exposure, this PAG generates an acid that should have very limited mobility as its anion is covalently linked to the polymer backbone. The NR profile for an unexposed bilayer that has not been PEB processed is shown in Figure 5. The reflectivity shows several interference fringes whose frequency is inversely proportional to the film thickness. Since the total film thickness approached the resolution limit for the neutron reflectometer, each fringe is defined with few data points, leading to a large uncertainty in the film thickness. Thus x-ray reflectivity (XR) was used to independently quantify the total film thickness. The difference in film thickness between XR and NR experiments was less than 5 nm, corresponding to a deviation of less than 3 % in the total film thickness. However from the x-ray measurements, only the total film thickness could be obtained due to insufficient x-ray contrast between the polymeric PAG and the PTBOCST. This was not the case for the NR measurements where the interface between the layers can be resolved. For the unexposed bilayer with no PEB, the interface was sharp with an interfacial width of 9.3 Å. This is slightly larger, but comparable to NR measurements for unprocessed PTBOST / PHOST bilayers.[13] Upon exposure to ultraviolet (UV) radiation, there is no significant change in the interfacial width without a PEB.

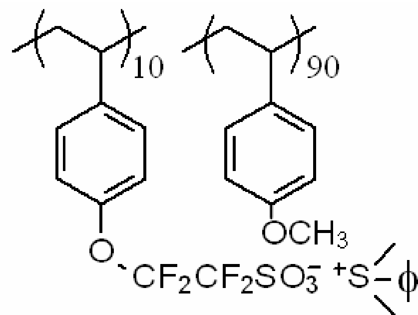

Figure 4. Structure of polymeric PAG

The composition profile was observed to undergo significant changes after exposure and baking at 90 °C. Figure 6 shows the NR profile after 2 min PEB. From a comparison between Figures 5 and 6, it is clear that the fringes persist to a much larger q for the unbaked sample. This is evidence for an increased NSLD gradient in the film after baking, through the broadening of the polymeric PAG / PTBOCST interface. From the fit of the NR in Figure 6, the interfacial width has increased from the 9.3 Å of the unbaked film to 190 Å after 2 min PEB at 90 °C. Additionally, the NSLD for the polymeric PAG appears to be reduced from 6.3×10^{-7} Å^{-2} to -8.4×10^{-7} Å^{-2}, indicative of a significant increase in the hydrogen composition. The reason for this apparent composition change within the polymeric PAG is unclear at this time. However as the PEB time is increased to 8 min, the NSLD for the polymeric PAG is further decreased to -1.5×10^{-6} Å^{-2}, supporting the concept of a compositional change in the polymeric PAG during the PEB. In addition to the change in NSLD, the interfacial width is further increased to approximately 500 Å after the 8 min PEB at 90 °C. The diffusion of the polymeric PAG can best be illustrated by examining the NSLD profiles obtained from the NR fits as shown in Figure 7. The scattering length density is shown as a function of distance from the silicon wafer interface (z). Thus, at $z < 0$ Å, the NSLD corresponds to silicon. At $z = 0$ Å, there is a sharp decrease in the NSLD, indicative of the sharp interface between silicon and polymeric PAG. Initially the polymeric PAG is approximately 800 Å thick. At $z \approx 800$ Å for the unbaked film, there is a sharp increase in NSLD corresponding to the dPTBOCST. The high NSLD is a result of the deuterium substitution on the t-BOC moiety. At $z = 2150$ Å (the total bilayer film stack thickness), the scattering length density decreases to zero corresponding to the dPTBOCST / air interface. After the PEB for either 2 min or 8 min, there is a substantial broadening of the bilayer interface and a decrease in the total film thickness. The change in film thickness is expected during the deprotection reaction.

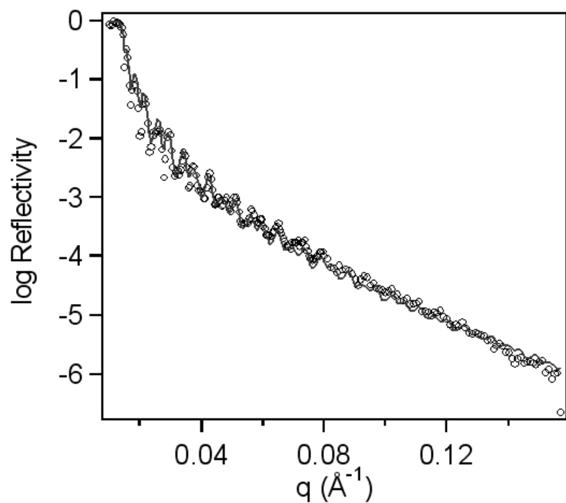

Figure 5. NR profile of polymeric PAG / PTBOCST bilayer sample without exposure or PEB processing (best fit of the data shown with solid line)

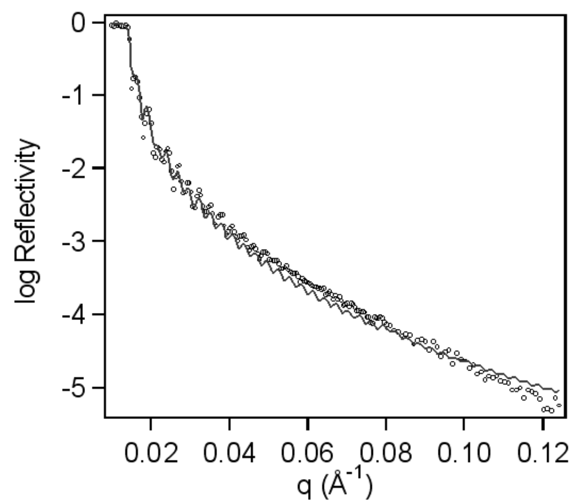

Figure 6. NR profile of polymeric PAG / PTBOCST bilayer sample after exposure and 2 min, 90 °C PEB. (best fit of the data shown with solid line)

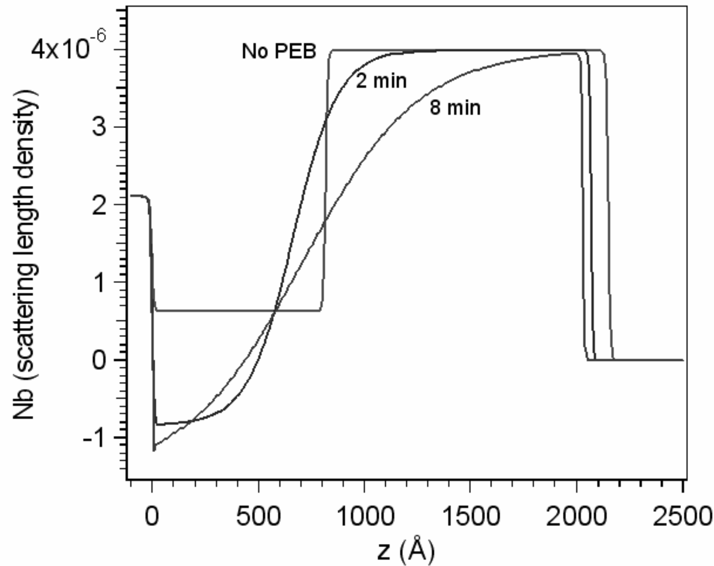

Figure 7. Neutron scattering length density profiles for three PEB conditions.

Another common formulation variable capable of altering diffusion-induced bias is the base additive loading. Increasing the amount of alkaline additives in the resist effectively decreases the initial acid concentration in exposed regions. A decreased acid concentration could reduce the driving force behind catalyst migration, but the main effect of base additives on diffusion is thought to be the scavengingeffect. The relatively low base concentrations in the resist have little impact in exposed regions (high acid concentration regions), but the relatively few acid molecules that diffuse into the unexposed regions react with the added base. Some initial work has suggested that the reaction between photoacid and base additives is not necessarily irreversible.[20] If this is indeed the case, the effect of base additives will not necessarily be linear and diffusion-induced bias can not be completely eliminated by adding base to the resist formulation. Figure 8 presents results from a series of bilayer experiments carried out at 90 °C in which the acid source layer contained 10 percent by mass of a nonaflate PAG and base (1-piperidineethanol) was added to the acid detector layer in varying quantities. The reported base ratios are based on a hypothetical 1 mol percent PAG loading in the detector layer (no PAG was actually added to the detector layer). Measured diffusion distances range from 50 nm for no added base to 20 nm for a 2:1 PAG to base ratio.

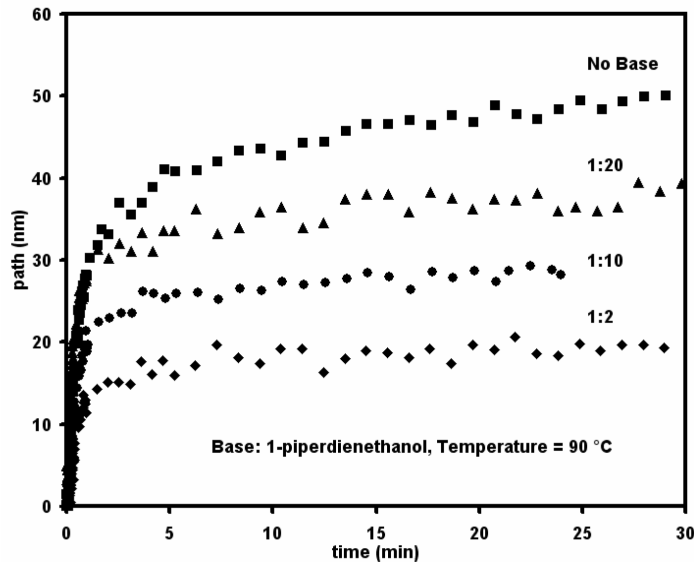

Figure 8. Bilayer diffusion distance for several relative concentrations of added base

There is, of course, a limit to how much base can be added to the photoresist formulation. Increasing the base concentration until it is on par with the generated acid will certainly reduce diffusion-induced bias, but it will also prevent the acid from catalyzing the necessary solubility-switching reactions in exposed regions. To avoid this problem, some have proposed incorporation of a base that is photodecomposable.[16,21] A base molecule that is destroyed upon exposure would allow higher overall base loadings and thus further limit diffusion bias. As of yet, no completely workable solution has been realized, but to some extent photodecomposable bases already exist in resist formulations due to ion metathesis occurring while the resist is still in the bottle. The issues of photodecomposable bases remain to be resolved.

CONCLUSIONS

All of the "Next Generation Lithography" techniques included in the Semiconductor Industry Association's Roadmap (excluding imprint-based methods) assume that high-resolution materials will be available to take advantage of the improved exposure capability that is expected of the "Next Generation" exposure tools.[22] These materials must be capable of not only very high resolution (< 50 nm), but also very high sensitivity to reduce the cost of ownership of the exposure tools and thereby maintain profitability. Unfortunately, evidence to date suggests that these two requirements are, to some extent, mutually exclusive in positive-tone chemically amplified materials. To date, the best resolution that has been demonstrated in a positive tone CAR is only marginally better than the 40 nm isolated trench that was reported over 15 years ago.[3] Examples of successfully printed sub-40 nm, nested line/space patterns in positive tone CARs are very rare. It appears that the mechanisms responsible for high sensitivity in these resists are intrinsically tied to the processes that result in diffusion-induced bias.

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REFERENCES

1. C. G. Willson, H. Ito, J. M. J. Frechet, T. G. Tessier, and F. M. Houlihan, *J. Electrochem. Soc.* **1986**,*133***,** 181-187.
2. C. G. Willson, in *Introduction to Microlithography*, edited by L. F. Thompson, C. G. Willson, and M. J. Bowden (American Chemical Society, Washington, D.C., 1994).
3. C. P. Umbach, A. N. Broers, C. G. Willson, R. Koch, and R. B. Laibowitz, *J. Vac. Sci. Technol. B* **1988**,*6***,** 319-322; C. P. Umbach, A. N. Broers, R. H. Koch, C. G. Willson, and R. B. Laibowitz, *IBM J. Res. Dev.* **1988**,*32***,** 454-461.
4. W. Hinsberg, F. Houle, M. I. Sanchez, J. Hoffnagle, G. Wallraff, D. R. Medeiros, G. Gallatin, and H. Cobb, *Proc. SPIE - Int. Soc. Opt. Eng.* **2003**,*5039***,** 1-14.
5. H. Ito, G. Breyta, D. Hofer, R. Sooriyakumaran, K. Petrillo, and D. Seeger, *J. Photopolym. Sci. Technol.* **1994**,*7***,** 433.
6. J. Hoffnagle, W. Hinsberg, M. I. Sanchez, and F. Houle, *J. Vac. Sci. Technol. B* **1999**,*17***,** 3306.
7. M. Switkes and M. Rothschild, *Proc. SPIE - Int. Soc. Opt. Eng.* **2002**,*4691***,** 459; M. Switkes and M. Rothschild, *J. Vac. Sci. Technol. B* **2001**,*19***,** 2353.
8. H. Solak, D. He, W. Li, F. Cerrina, B. H. Sohn, X. M. Yang, and P. Nealey, *Proc. SPIE - Int. Soc. Opt. Eng.* **1999**,*3676***,** 278.
9. T. H. Fedynyshyn, J. Thackeray, J. Georger, and M. Denison, *J. Vac. Sci. Technol. B* **1994**,*12***,** 3888; J. Sturtevant, S. Holmes, and P. Rabidoux, *Proc. SPIE - Int. Soc. Opt. Eng.* **1992**,*1672***,** 114.
10. M. D. Stewart, M. H. Somervell, H. V. Tran, S. V. Postnikov, and C. G. Willson, *Proc. SPIE - Int. Soc. Opt. Eng.* **2000**,*3999***,** 665-674.
11. S. V. Postnikov, M. D. Stewart, H. Vi Tran, M. A. Nierode, D. R. Medeiros, T. Cao, J. Byers, S. E. Webber, and C. G. Wilson, *J. Vac. Sci. Technol. B* **1999**,*17***,** 3335-3338.
12. M. D. Stewart, S. V. Postnikov, H.-V. Tran, D. R. Medeiros, M. A. Nierode, T. Cao, J. Byers, S. E. Webber, and C. G. Willson, *Amer. Chem. Soc., Polym. Mat. Sci. Eng.* **1999**,*81***,** 58-59.

[13] E. K. Lin, C. L. Soles, D. L. Goldfarb, B. C. Trinque, S. D. Burns, R. L. Jones, J. L. Lenhart, M. Angelopoulos, C. G. Willson, S. K. Satija, and W.-l. Wu, *Science* **2002**,*297***,** 372-375.
[14] R. L. Jones, T. Hu, E. K. Lin, W.-l. Wu, D. L. Goldfarb, M. Angelopolous, B. C. Trinque, G. M. Schmid, M. D. Stewart, and C. G. Willson, *J. Polym. Sci. Pt. B - Polym. Phys.* **2004**,*In press*.
[15] X. Shi, *J. Vac. Sci. Technol. B* **1999**,*17***,** 350.
[16] W. D. Hinsberg, F. A. Houle, M. I. Sanchez, M. E. Morrison, G. M. Wallraff, C. E. Larson, J. A. Hoffnagle, P. J. Brock, and G. Breyta, *Proc. SPIE - Int. Soc. Opt. Eng.* **2000**,*3999***,** 148.
[17] F. A. Houle, W. D. Hinsberg, M. I. Sanchez, and J. A. Hoffnagle, *J. Vac. Sci. Technol. B* **2002**,*20***,** 924-931; S. L. Ablaza, J. F. Cameron, G. Y. Xu, and W. Yueh, *J. Vac. Sci. Technol. B* **2000**,*18***,** 2543-2550.
[18] M. D. Stewart, H. V. Tran, G. M. Schmid, T. B. Stachowiak, D. J. Becker, and C. G. Willson, *J. Vac. Sci. Technol. B* **2002**,*20***,** 2946-2952.
[19] B. C. Trinque, *Ph.D. Dissertation*, The University of Texas at Austin (2003).
[20] T. B. Michaelson, A. T. Jamieson, A. R. Pawloski, J. Byers, and C. G. Willson, *Proc. SPIE - Int. Soc. Opt. Eng.* **2004**,*These proceedings*.
[21] M. Padmanaban, J.-B. Bae;, M. Cook, W.-K. Kim;, A. Klauck-Jacobs, T. Kudo, M. D. Rahman, R. R. Dammel, and J. D. Byers, *Proceedings of the SPIE - The International Society for Optical Engineering* **2000**,*3999***,** 1136-1146; O. Nalamasu, F. M. Houlihan, R. A. Cirelli, A. G. Timko, G. P. Watson, R. S. Hutton, J. M. Kometani, E. Reichmanis, A. Gabor, A. Medina, and S. Slater, *J. Vac. Sci. Technol. B* **1998**,*16***,** 3716-3721; S. Funato, N. Kawasaki, Y. Kinoshita, S. Masuda, H. Okazaki, M. Padmanaban, T. Yamamoto, and G. Pawlowski, *Proceedings of the SPIE - The International Society for Optical Engineering* **1996**,*2724***,** 186-195.
[22] *International Technology Roadmap for Semiconductors: Lithography*, Semiconductor Industry Association (2003).