348 *Chem. Mater.* **1993,** *5,* 348–356

Airborne Contamination of a Chemically Amplified Resist. 1. Identification of Problem

Scott A. MacDonald,* William D. Hinsberg, H. Russell Wendt,
Nicholas J. Clecak, and C. Grant Willson

*IBM Research Division, Almaden Research Center, 650 Harry Road,
San Jose, California 95120-6099*

Clinton D. Snyder

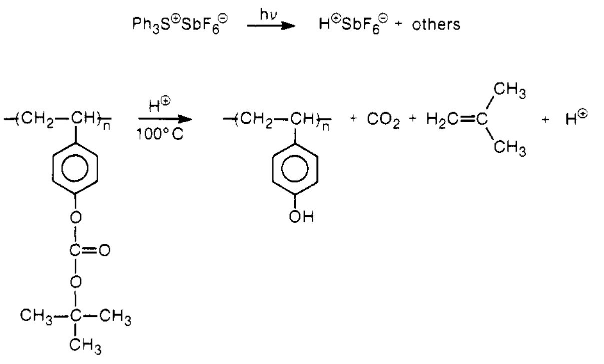
IBM Corporation, 5600 Cottle Road, San Jose, California 95193

Received November 5, 1992. Revised Manuscript Received December 31, 1992

The lithographic performance of a chemically amplified resist is severely degraded by vapor from organic bases. This effect is very pronounced and can be observed when the coated wafers stand for only a few minutes in air containing parts per billion (ppb) levels of an organic base. In resist systems derived from poly[4-((*tert*-butyloxycarbonyl)oxy)styrene], the contamination induced effect takes two general forms. When processed in the negative tone, the UV exposure dose required to obtain the correct linewidth increases. When processed in the positive tone, a "skin" forms at the resist–air interface. Both effects are caused by the photogenerated acid being neutralized by the airborne organic base. A wide variety of commonly used materials liberate trace amounts of volatile amines and degrade resist performance. We have quantified the incorporation of one such airborne contaminant, *N*-methylpyrollidone (NMP), by thin polymer films. NMP labeled with ^{14}C was introduced at a concentration of 10 ppb into a stream of purified air and the films of interest were allowed to stand in the airstream for a predetermined time under controlled conditions. This method allows for determining NMP uptake rate, correlating lithographic performance with absorbed NMP content, and studying the effects of film thickness or composition on absorption rates.

Introduction

In the early 1980s, Fréchet, Ito, and Willson described the use of photogenerated acid to yield a sensitive, dual-tone DUV resist.[1–4] The chemistry of this system (known as chemical amplification) is shown in Figure 1 and consists of two distinct steps: (1) photolysis of an onium salt to generate acid; (2) acid-catalyzed thermolysis of a *tert*-butylcarbonate to yield a phenolic hydroxyl group. The basic concepts behind chemical amplification have been extended to several other imaging systems[5] and currently represent the predominant approach to designing modern DUV/E-beam/X-ray resists. This class of radiation sensitive imaging materials has been recently reviewed by Reichmanis and co-workers.[6]



PBOCST

Figure 1. Chemically amplified resist chemistry of the PBOCST/Ph_3SSbF_6 system.

Chemically amplified resists not only are being investigated by resist research groups but are also being used by manufacturing and development groups. In 1990, Maltabes et al. described using the poly[4-((*tert*-butyloxycarbonyl)oxy)styrene] (PBOCST) resist system and DUV lithography to manufacture 1-Mbit DRAM devices.[7] Also, in 1990 and 1992, Holmes et al. described the use of a proprietary DUV chemically amplified resist on a 16-Mbit DRAM, pilot-line operation.[8,9]

While evaluating the PBOCST/onium salt system for use on the manufacturing floor, we observed that the lithographic characteristics of freshly coated wafers dif-

---

(1) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012–1018.

(2) Ito, H.; Willson, C. G. In *Polymers in Electronics*; ACS Symposium Series No. 242; Davidson, T., Ed.; American Chemical Society: Washington, DC, 1984; pp 11–23.

(3) Ito, H.; Willson, C. G.; Fréchet, J. M. J. U.S. Patent 4,491,628, 1985.

(4) Fréchet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit Eng.* **1982**, 260.

(5) *Polymers in Microlithography: Materials and Processes*; ACS Symposium Series No. 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington, DC, 1989; pp 27–114.

(6) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991**, *3*, 394–406.

(7) Maltabes, J. G.; Holmes, S. J.; Morrow, J. R.; Barr, R. L.; Hakey, M.; Reynolds, G.; Brunsvold, W. R.; Willson, C. G.; Clecak, N. J.; MacDonald, S. A.; Ito, H. Advances In Resist Technology and Processing VII. *Proc. SPIE* **1990**, *1262*, 2–7.

(8) Holmes, S.; Levy, R.; Bergendahl, A.; Holland, K.; Maltabes, J.; Knight, S.; Korris, K. C.; Poley, D. Optical/Laser Microlithography III. *Proc. SPIE* **1990**, *1264*, 61–70.

(9) Holmes, S.; Bergendahl, A.; Dunn, D.; Hakey, M.; Holland, K.; Horr, R.; Humphrey, D.; Knight, S.; Norris, K.; Poley, D.; Rabidoux, P.; Sturtevant, J.; Writer, D.; Electron-Beam, X-Ray, and Ion-Beam Submicrometer Lithographies for Manufacturing II. *Proc. SPIE* **1992**, *1671*, 57–75.

0897-4756/93/2805-0348$04.00/0

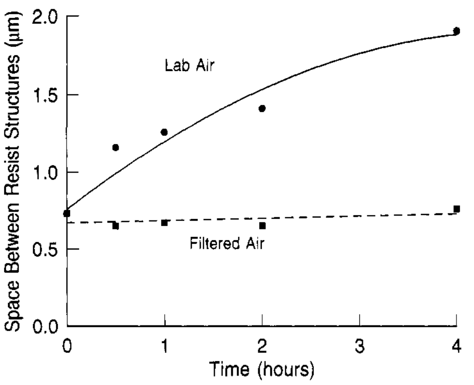


Figure 2. Linewidth change for negative tone PBOCST/Ph$_3$SSb$_6$ coated wafers that stood in two environments: (●) laboratory air; (■) carbon-filtered air.

fered from wafers which were exposed 8, 12, or 24 h after coating. When processed in the negative tone, this change in lithographic performance appeared as a decrease in DUV exposure sensitivity. That is, the longer the coated wafers stood before DUV exposure, the greater the dose required to obtain correct image size. Conversely, if the DUV exposure dose was held constant, the longer the coated wafers stood, the more the image size changed. This change in linewidth with time can be large ($\sim$0.4-µm shift in a nominal 1-µm image in 30 min) and is shown in Figure 2 (●). When processed in the positive tone, the performance characteristics changed if the coated wafers were allowed to stand before the DUV exposure. For the positive tone system, after a short delay between coating and DUV exposure, a "lip" formed at the top of the relief image. A longer delay yielded a thin "skin" at the resist-air interface. This thin skin is shown in Figure 3.

The chemistry of this resist system, shown in Figure 1, suggests a reason for this observed degradation in resist performance. The central feature of any chemically amplified resist is the use of a small number of photogenerated acid molecules to initiate a catalytic reaction. The catalytic chain length (or gain) associated with these systems is substantial. McKean et al. have reported that each acid molecule cleaves approximately 1000 carbonate units.[10] Because of the long catalytic chain length, any basic impurity which reduces the activity of the photogenerated acid will have a correspondingly large effect that also degrades lithographic performance. Hence one explanation for the data in Figure 2 (●) is that after standing, the coated resist films contain a basic impurity which inhibits the photogenerated acid. Furthermore, since the linewidth change in Figure 2 (●) increases with time, it appears that the basic inhibitor concentration within the film also increases with time. This observation is consistent with resist films absorbing the basic inhibitor from the surrounding environment.[11]

This paper is divided into two sections. In the first section we will show that storing coated resist films in conventional clean room air degrades their lithographic performance. However, storing the coated resist films in clean room air that has been scrubbed by a high-efficiency carbon filter preserves lithographic performance and yields a stable manufacturing process. We will present data supporting the theory that the carbon filter removes volatile organic bases from the clean room air.

While it is difficult to know which deleterious organic vapors are present at the ppb level in clean room air, examining the list of chemicals typically used in semiconductor production provides several likely candidates. One such material, 1-methyl-2-pyrollidone (NMP) is widely used for casting and stripping the organic films used in microelectronic fabrication. NMP was reported by our laboratory to degrade the performance of an acid catalyzed, chemically amplified resist.[12] Our observation that ppb levels of NMP vapor degrade chemically amplified resist systems is supported by similar studies at AT&T Bell Laboratories.[13] In the second section of this paper we will describe using radiolabeled 1-[^{14}C]methyl-2-pyrollidone (NMP*) and standard radiotracer techniques to determine absolute amounts of absorbed NMP. A series of experiments designed to quantify amounts of airborne contaminant absorbed by resist films, to determine the kinetics of NMP uptake, and to characterize the effects of polymer film thickness and composition are described.

Experimental Section

Unless stated otherwise, all experiments were performed using 1.0-µm-thick polymer films. The films were spin-coated on 125-mm-diameter silicon wafers and post-apply baked on a hotplate at 100 °C for 5 min. Coatings were applied immediately prior to placement in the contaminated airstream.

The experimental apparatus used for the dynamic contamination experiments is shown schematically in Figure 4. Clean air is drawn from outside the building, through existing ductwork, and is passed through a high-efficiency activated carbon filter at a constant air flow of 60 std ft^3/min. The airstream is split in half at a tee-fitting downstream from the filter. A low flow of NMP*-laden nitrogen ($\sim$70 mL/min, prepared by passage through a glass U-tube containing liquid NMP* dispersed on glass beads) is added to one half of the airstream, which then passes through a 20-ft length of flexible metal tubing to ensure mixing. The other half of the airstream is configured identically but without provision for adding a contaminant vapor, and serves as a reference channel. Both air channels terminate in vertical metal chimneys of such size that a wafer carrier holding coated silicon substrates can be placed within. The final concentration of NMP* in the doped airstream can be controlled by varying the nitrogen flow rate, and is calibrated by measuring weight loss from the U-tube over 24 h. In the experiments described here, the final concentration of NMP* in the doped airstream was 10 ppb. The airstream doped with *N,N*-dimethylaniline was prepared in the same fashion.

Radiolabeled 1-[^{14}C]methyl-2-pyrollidone was obtained from Sigma Chemicals as a solution in hexane. After transfer to the U-tube, unlabeled NMP was added and the hexane was evaporated to provide a final specific activity measured to be 2.71×10^6 dpm/mg.

The experimental protocol for the radiolabeled studies was as follows. After allowing the air-handling apparatus to stabilize for at least 30 min, a series of coated wafers was prepared and placed in the NMP*-laden airstream. After a timed period the wafers were withdrawn. The coating on each wafer was stripped with 5 mL of an appropriate solvent (typically propylene glycol monomethyl ether acetate). The wafer and stripping vessel were then rinsed twice with aliquots of Aquassure LSC cocktail (NEN, Dupont). The level of ^{14}C activity in the combined stripping

---

(10) McKean, D. R.; Schaedeli, U.; MacDonald, S. A. *J. Polym. Science: Part A: Polym. Chem. Ed.* **1989**, *27*, 3927–3935.

(11) 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. Advances in Resist Technology and Processing VIII. *Proc. SPIE* **1991**, *1466*, 2–12.

(12) Hinsberg, W. D.; MacDonald, S. A.; Clecak, N. J.; Snyder, C. D. Advances in Resist Technology and Processing IX. *Proc. SPIE* **1992**, *1672*, 24–33.

(13) Nalamasu, O.; Cheng, M.; Timko, A.; Pol, V.; Reichmanis, E.; Thompson, L. *J. Photopolym. Sci. Technol.* **1991**, *4*, 299–317.

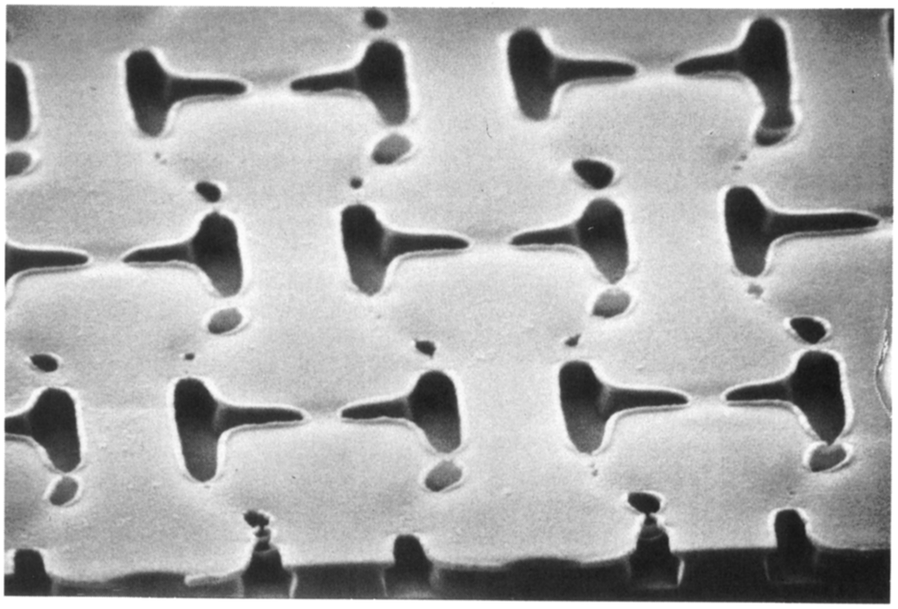


Figure 3. Positive tone image that was processed with a delay time. Note formation of a "skin" at the resist–air interface.

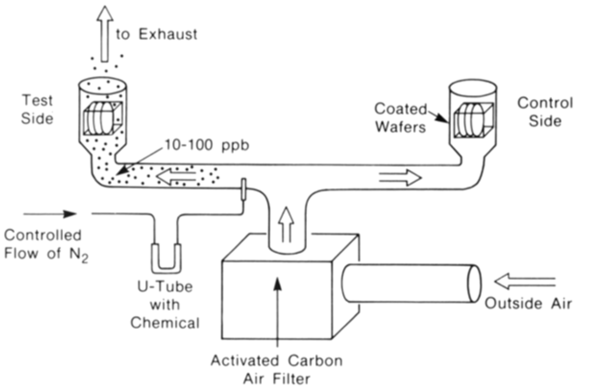


Figure 4. Dynamic flow system used to generate contaminated air.

liquids was then measured by liquid scintillation counting. All measurements were made in duplicate. In general, for all materials studied, the difference between duplicate samples within a run was less than 10%.

Results and Discussion

(I) Resist Contamination by Clean Room Air.

Carbon Filtration of Clean Room Air. Clean room air contains many basic substances that could be responsible for the degradation in lithographic performance. Since the typical clean room operates with a relative humidity of 40%, water is a prime suspect. Water is a stronger base than the *tert*-butylcarbonate group; hence if water was absorbed from the air and present in the resist film, it would effectively compete for the photogenerated acid. To evaluate the possibility that atmospheric water was responsible for the linewidth control problem described in the introduction, we allowed PBOCST resist films to stand in a atmosphere containing tritiated water vapor and thereby quantified water absorption. As described in a previous report, the water content of the PBOCST films did not increase after 24 h in the test chamber, yet the lithographic performance declined.[11] Since this specific chemically amplified resist does not absorb water from the environment, atmospheric water can not be responsible for the line-width change observed in Figure 2.

Water is not the only basic substance commonly found in air. A variety of volatile nitrogen-containing compounds may also be present. Semiconductor device manufacturing processes use a variety of nitrogen containing reagents which may generate volatile basic compounds. For example, a tetramethylammonium hydroxide (TMAH) solution (commonly used as a metal-ion-free developer) has a distinctly "fishy" aroma due to volatile alkylamines. Hexamethyldisilazane (HMDS) is often used as a priming agent to improve the adhesion of organic films to silicon wafers. Hot NMP is commonly used to strip off organic films used in the lithographic process. Hence, there is good reason to suspect that an airborne organic base may be responsible for the observed linewidth shift.

To investigate this possibility, we have used a high-efficiency carbon filter apparatus as a source of pure air to conduct environmental studies. The carbon filtration unit consists of a fan, an active carbon filter bed, and a HEPA filter. Laboratory air is drawn into the filter housing and passed over the specially designed, low-leakage active carbon bed to remove organic components. The air then passes through a series of particle filters before it is ready for use. The specific carbon filter unit that we used was originally designed to filter the air in a magnetic disk file; however, the use of active carbon filters to remove organic material from air is a well-established pollution control technique.

Coated wafers that are allowed to stand in carbon filtered air behave differently from coated wafers which stand in conventional clean room air. For this study, 125-mm-diameter silicon wafers were coated with the PBOCST/Ph_3SSbF_6 resist and baked. One set of coated wafers was allowed to stand under a laminar flow hood. The other set of wafers was placed in an open container approximately one meter away. This container was continuously purged with clean room air that passed through the carbon filtration unit (see Figure 5). At various time intervals, one coated wafer from each set was removed from its test environment and subjected to the standard lithographic process. The linewidth of the developed image was measured by SEM (five sites per wafer) and the average values are shown in Figure 2. The data in Figure 2 show that the two test environments are substantially different. Wafers which stood under the laminar flow hood exhibit a rapid linewidth change with time, while wafers

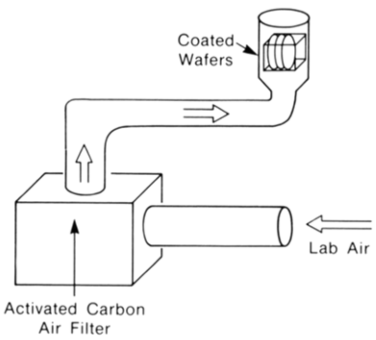


Figure 5. Schematic of carbon air filtration system used to produce the test environment found in Figure 2.

which stood in the carbon filtered air show constant linewidth. The data in Figure 2 are consistent with the theory proposed in the Introduction, that an airborne organic contaminant is responsible for the observed linewidth shift.

The linewidth shown in Figure 2 is for the "space", or gap, between two resist structures in the PBOCST/onium salt negative tone system. The following analysis suggests that the "space" should increase if a basic organic contaminant is absorbed from the surrounding environment. Consider exposing a film of the PBOCST/onium salt resist to DUV light through a mask containing an equal line/space pattern. Acid will be generated in the exposed areas. The postexposure-bake will initiate the acid-catalyzed cleavage of *tert*-butyl carbonate. Finally, solvent development with anisole will remove the unexposed regions of the film. A basic contaminant absorbed by the film will inhibit the acid-catalyzed cleavage reaction and thereby cause the exposed regions to shrink. It follows that as the exposed region gets smaller, the unexposed region will become larger. Since solvent development removes the unexposed areas, base contamination should result in smaller resist structures surrounded by larger "spaces". This is consistent with the data shown in Figure 2.

Effect of Artificially Generated Contaminated Air. The data in the previous section argue that the carbon filtration unit is removing some airborne organic contaminant but do not identify the chemical nature of that contaminant. We have addressed this issue by allowing resist-coated wafers to stand in air that was intentionally doped with organic vapor. A variety of compounds were screened with a static contamination test chamber. In these experiments, a resist-coated 125-mm-diameter wafer was allowed to stand for 30 minutes in a closed two liter vessel containing 10 μL of the test reagent. Assuming that all of the test reagent evaporates, a density of 1.0 g/mL, and a molecular weight of 100, the test chamber atmosphere should contain approximately 1000 ppm of contaminant. The coated wafer was then subjected to the standard lithographic process and examined for linewidth changes. The results were clear. Common solvents such as acetone, ethylacetate, or pentane did not induce linewidth changes. But amines such as triethylamine, pyridine, or *N*-methylmorpholine induced massive changes in lithographic performance. In fact, the coated wafers which were treated with amine vapor did not produce any image at a standard UV exposure dose.

The static test chamber setup is useful for gross screening experiments but not for quantitative work. For this purpose, a dynamic system was constructed to examine contaminant concentrations in the part per billion (ppb) range. This test chamber is shown in Figure 4. In this test chamber, a carbon filtration unit is used to provide a source of clean air. The contaminating agent is placed into the glass U-tube and carried into the carbon filtered air stream by nitrogen gas. The contaminant concentration is calculated from the weight loss of the glass U-tube over 24 h. A key feature of the dynamic flow system is the ability to deliver a slow contaminant flow rate (typically 50–200 mg/24 h) into a fast-moving stream of carbon-filtered air.

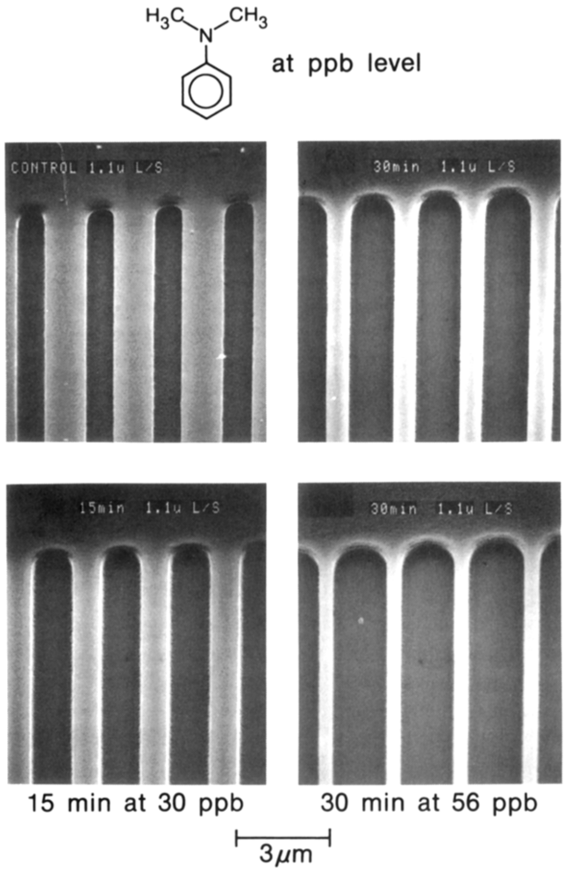


Figure 6. SEM photographs of negative tone image after a wafer coated with PBOCST/Ph_3SSbF_6 stood in *N*,*N*-dimethylaniline-contaminated air.

We have used this dynamic system to prepare contaminant concentrations in the ppb range. Even at this low concentration, amines have a potent effect on coated resist wafers. Figure 6 shows the results of allowing 125-mm-diameter wafers coated with the PBOCST/Ph_3SSbF_6 resist to stand in air containing 30 ppb of *N*,*N*-dimethylaniline. In this study, coated wafers stood in the contaminated air stream for 15 or 30 min. They were removed from the dynamic test chamber, exposed on a 0.35 NA, 1X UltraStep X-248E step-and-repeat system (2.8 mJ/cm^2), baked and developed with anisole. The SEM photographs in Figure 6 show the linewidth shift in a nominal 1.1-μm image for these wafers. Increasing the contaminant concentration to 56 ppb increases the linewidth shift. Figure 6 shows SEM photographs of coated wafers which stood for 30 min in 30 and 56 ppb *N*,*N*-dimethylaniline. Note that 30 min of 56 ppb severely alters image size. The data in Figure 6 are consistent with the theory proposed in the Introduction, that a basic, airborne organic contaminant is responsible for the observed linewidth shift.

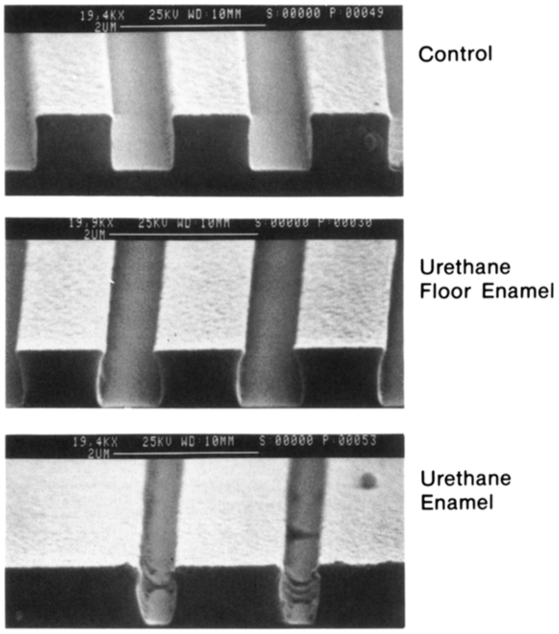


Figure 7. SEM photographs of positive tone image after a coated wafer stood for 15 min in a desiccator containing paint fumes.

Our observation that ppb levels of amine vapor degrade acid-catalyzed chemically amplified resists has been confirmed by another laboratory. Nalamasu et al. (AT&T Bell labs) reported that an atmosphere contamining 15 ppb HMDS severely degraded a positive tone, chemically amplified resist.[13,14]

Effect of Construction Materials. Clean rooms contain numerous sources of volatile amine contaminants in addition to the chemicals used to manufacture semiconductor devices. Common cleaning solutions often contain ammonia, and amines are used as curing reagents in a variety of paints, adhesives, and sealants. Since vapors emanating from curing construction materials are difficult to quantify, we have used a static test chamber to screen for detrimental effects. For this work, a sample of construction material was allowed to stand in a small desiccator for 2 h, to generate a contaminated environment. A coated wafer was placed into the desiccator for 15 min, removed, and processed to yield a positive tone image. This image was examined for linewidth change as compared to a control wafer. The SEM photographs in Figure 7 show the effect of urethane paint fumes. Note that the wafer treated with vapor from urethane enamel shows a linewidth shift and the formation of a "lip" at the resist–air interface.

This technique has been used to screen several construction materials and the results are shown in Figure 8. In this study, "pass" means that after 15 minutes in the contaminated environment, the final image was within 10% of an uncontaminated control. The test chamber used to generate the data in Figure 8 contains an unknown, but undoubtedly high contaminant level. Hence it represents a worst-case-analysis for construction materials. However, the data in Figure 8 clearly show that a wide variety of common materials generate detrimental vapor.

MATERIAL	RESULT
Fresh Urethane Paint	Fail
GE Silicone II Caulking	Fail
Dow Corning 732 Sealant	Fail
PVC Glue	Fail
Floor Bond 600 Adhesive	Fail
Safety Label Adhesive	Pass
Freon TF	Pass

Figure 8. Construction materials tested in a static chamber. A "pass" result means that the final image size of the contaminated wafer was within 10% of an uncontaminated control.

While we have not identified the specific contaminant emanating from each of these construction materials, the general observation that they can liberate deleterious vapor has significant, practical implications. For example, the walls of the hallway housing the air-intake for our DUV exposure system were painted as part of routine building maintenance. This resulted in "fresh paint fumes" flowing through the DUV exposure system which severely degraded the performance of the PBOCST/onium salt resist. As a consequence, we were forced to suspend all lithographic experiments in the laboratory until the paint had cured and the paint fumes were gone.

Effect of Localized Air Filtration. In this paper we have demonstrated that carbon filtration of clean room air improves linewidth control, presumably by removing volatile organic bases from the air. One way to transfer this observation to the manufacturing floor would be to pass all clean room air through carbon filters. However, given the size of most manufacturing lines, this simple approach is not feasible. A more practical approach is to filter only the air surrounding the coated wafers.

In the 1-Mbit DRAM process described by Maltabes,[7] there are only two process steps in which the coated wafers require a carbon filtered environment. First, wafers that have been coated and baked need a filtered environment before exposure. Second, wafers in the exposure tool input cassette require carbon filtered air. Thus this process is amenable to localized air filtration. To implement this process, we prepared a "holding-box" (approximately 1 m × 1 m × 1 m) attached to a carbon filtration unit. This provided a contaminant-free storage environment for coated wafers awaiting UV exposure. The input cassette area of the DUV exposure tool was enclosed with a polycarbonate box that was slightly larger than a standard 25-wafer cassette. This polycarbonate box was attached to a carbon filtration unit and purged continuously with contaminant-free air. Filtering the air at these two locations dramatically improved the lithographic process. Specifically, the observed linewidth shift of the filtered process was only 0.07 μm for a nominal 1.0-μm image in 24 h, whereas in Figure 2 an unfiltered process exhibited a linewidth shift of 0.4 μm in 30 min.

The 1-Mbit DRAM semirecessed oxide level was manufactured with the PBOCST/Ph_3SbSbF_6 and the localized carbon filtration process. The resist imaging step required defining a 0.9-μm image (using a Perkin-Elmer Micralign 500) in a 1.6-μm-thick layer of resist. The throughput of this process was 100 wafers/h, while the raw cycle time through the exposure tool was approximately 20 s/wafer. This allowed us to run 600 wafer-starts/day/Micralign-500 without stressing the system. Rework was held to 1.5% and the photolimited yield (KLA) was 97%.[11]

---

(14) Nalamasu, O.; Reichmanis, E.; Cheng, M.; Pol, V.; Kometani, J.; Houlihan, F.; Neenan, T.; Bohrer, M.; Mixon, D.; Thompson, L.; Takemoto, C. Advances in Resist Technology and Processing VIII. *Proc. SPIE* **1991**, *1466*, 13–25.

Other Approaches to Excluding Contaminants. Another approach to excluding airborne basic contaminants from the resist film is to overcoat the resist with a barrier layer. For this two-layer approach to work, the barrier layer must be optically transparent, compatible with the acid-catalyzed chemistry, able to keep airborne basic contaminants from reaching the resist, and soluble in the developing solution. Workers from both IBM[9,15] and AT&T Bell Laboratories[13,14,16] have described using such an overcoat layer to protect positive-tone, acid-catalyzed chemically amplified resists. While neither of these two groups has described the exact chemical structure of the overcoat, the AT&T material appears to be a copolymer derived from poly(methacrylic acid).[14,16,17]

No matter which approach one uses to exclude airborne basic contaminants from the resist film, it is important to protect the film from the initial coating step until the acid-catalyzed chemistry has been completed. Figure 2 showed the deleterious effect of allowing coated resist films to stand in laboratory air and absorb atmospheric base prior to UV exposure. However, since the atmospheric contaminant interacts with the photogenerated acid, it is also harmful to allow contamination to occur between UV exposure and the postexposure-bake step. Other published reports of airborne contamination have focused on the time interval between UV exposure and the postexposure-bake step. Schwartzkopf et al. allowed UV exposed PBOCST films to stand for 1 h before the postexposure-bake step, in laboratory air and in closed containers.[18] This group observed a greater sensitivity loss for those samples stored in laboratory air, compared to samples stored in closed containers. Nalamasu et al. examined the post-exposure-delay properties of a positive tone system based on poly(*tert*-butyloxycarbonyloxy)styrene sulfone).[13] This group observed that storing UV exposed films in a chamber containing 15 ppb HMDS reduced UV sensitivity by at least a factor of 2 and severely degraded image quality.

Finally, it should be noted that not all acid-catalyzed resist systems exhibit this strong, postexposure-delay effect. Resist systems using an acid-catalyzed cross-linking mechanism have been reported to exhibit enhanced stability. Allen et al. have described a negative tone, acid-catalyzed DUV resist that exhibits no linewidth shift, even with delays as long as 23 h.[19] Röschert et al. have described a similar, negative-tone system that shows only minimal profile change (examining a 0.35-μm line/space image) after a 24-h delay.[20]

(II) Quantitation of Airborne Contamination by ^{14}C NMP. *Rates of NMP Uptake from a 10 ppb Airstream.* As previously mentioned, NMP is commonly used in semiconductor manufacturing, and its vapor has been shown to degrade acid-catalyzed resist systems. With this in mind, we have prepared an airstream (using the apparatus shown in Figure 4) containing 10 ppb of 1-[^{14}C]-methyl-2-pyrollidone (NMP*) and used radiochemical analysis to quantify the incorporation of this contaminant into resist films. Figure 9 displays the amounts of NMP* absorbed onto coated and uncoated 125-mm-diameter silicon wafers as a function of time in the NMP*-doped airstream. The amount adsorbed by a bare silicon wafer is small and is essentially constant over 30 min. However, applying a 1.0-μm film of PBOCST resist containing Ph_3SSbF_6 to the silicon substrate leads to a sharp increase in the rate of NMP uptake. After 10 min, a bare silicon wafer has adsorbed only 20 ng of NMP*, while the PBOCST-coated wafter has absorbed 450 ng of NMP*. This amount, corresponding to about 30 parts NMP in 10^6 parts of polymer on the wafer, is sufficient to cause noticeable degradation in resist properties: lithographic evaluation of PBOCST resist shows significant linewidth shifts (~0.3-μm shift in a 1.0-μm feature) after 10 min in an airstream containing 10 ppb NMP.

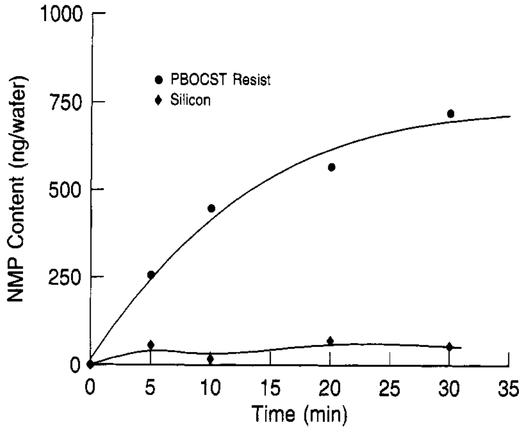


Figure 9. Absorbed NMP vs time in NMP-doped airstream: (●) PBOCST resist coated on to 125-mm silicon wafer; (♦) 125-mm silicon wafer.

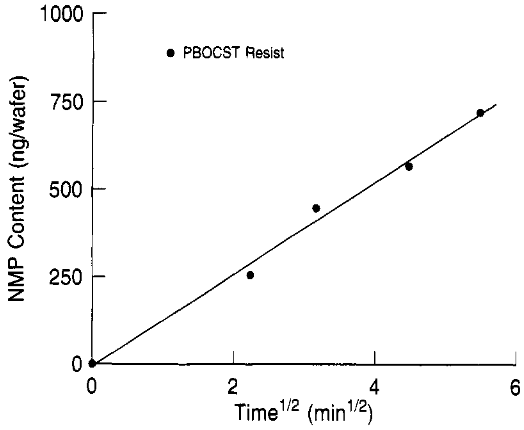


Figure 10. Absorbed NMP vs (time)$^{1/2}$ in NMP-doped airstream for the PBOCST resist.

From Figure 9, the total amount of NMP* absorbed by a PBOCST film increases with time, but in a nonlinear manner. For the case where the permeating species is a small molecule at low concentration diffusing in a glassy polymer film below its T_g, the diffusion process is expected to be Fickian.[21] If Fickian diffusion kinetics apply, then

---

(15) Sturtevant, J.; Holmes, S. J.; Rabidoux, P. Advances in Resist Technology and Processing IX. *Proc. SPIE* **1992**, *1672*, 114–124.

(16) Nalamasu, O.; Reichmanis, E.; Hanson, J. E.; Kanga, R. S.; Heimbrook, L. A.; Emerson, A. B.; Baiocchi, F. A.; Vaidya, S. *Polym. Eng. Sci.* **1992**, *32*, 1565–1570.

(17) Chandross, E. A.; Nalamasu, O.; Recihmanis, E.; Taylor, G. N.; Thompson, L. F. European Patent Application, 0,476,840,A1, 1992.

(18) Schwartzkopf, G.; Naizy, N. N.; Das, S.; Surendran, G.; Covington, J. B. Advances in Resist Technology and Processing VIII. *Proc. SPIE* **1991**, *1466*, 26–38.

(19) Allen, M.; Calabrese, G.; Lamola, A.; Orsula, G.; Rajaratnam, M.; Sinta, R.; Thackeray, J. *J. Photopolym. Sci. Technol.* **1991**, *4*, 379–387.

(20) Röschert, H.; Dammel, R.; Eckes, C.; Kamiya, K.; Meier, W.; Przybilla, K. J.; Spiess, W.; Pawlowski, G. Advances in Resist Technology and Processing IX. *Proc. SPIE* **1992**, *1672*, 157–171.

(21) Vrentas, J.; Duda, J. Diffusion. In *Encyclopedia of Polymer Science and Technology*; Wiley-Interscience: New York, 1986; Vol. 5, p 63.

RESIST A

TIME IN CHAMBER (min)	FILM THICKNESS Å	AMT NMP ABSORBED (ng/wafer)
15	10,000	455
	1000	163
60	10,000	969
	3500	374

RESIST B

TIME IN CHAMBER (min)	FILM THICKNESS Å	AMT NMP ABSORBED (ng/wafer)
15	10,000	583
	1000	675

Figure 11. Absorbed NMP vs film thickness for resists A and B.

the total amount of contaminant absorbed should increase linearly with the square root of elapsed time.[22] Figure 10 shows the PBOCST/NMP* uptake data from Figure 9, plotted in this manner. The plot of NMP* vs $(\text{time})^{1/2}$ is linear, within the precision of the experiment, consistent with a Fickian diffusion process.

Depth Distribution of Absorbed NMP in the Polymer Film. One may be able to better understand how airborne contamination affects lithographic imaging by examining the depth distribution of absorbed NMP within resist films. Three distinct depth distributions are considered:

(1) A uniform distribution, i.e., one in which the NMP concentration is the same throughout the bulk of the film. This situation can occur if the diffusion of NMP through the film is relatively fast, as compared to the time the film stands in the contaminated air stream.

(2) A nonuniform distribution where the absorbed NMP is concentrated in a thin region near the air–film interface. This will occur if diffusion of NMP through the film is relatively slow on the time scale of the experiment.

(3) A depth distribution of NMP that is somewhere between these two extremes.

One way to differentiate between these three depth distributions is to determine how the total amount of absorbed NMP varies with changes in film thickness. If the total NMP content changes in proportion to the film thickness, then the depth distribution within the film must be uniform. However, if the NMP content is independent of the film thickness, then the absorbed material is concentrated near the interface. The NMP depth distribution for two resist systems was examined by altering film thickness. The two resist systems examined are (A) a standard PBOCST resist containing 5 wt % Ph_3SSbF_6 and (B) an experimental positive-tone chemically amplified resist composed of a copolymer incorporating the *t*-BOC–styrene monomer and 5 wt % Ph_3SSbF_6.

For each resist, films of 1.0- and 0.1-μm thickness were placed in the NMP*-doped airstream for 15 min. The amounts of NMP* absorbed by each film are given in the table in Figure 11. For resist A, the amount of absorbed NMP* is a function of thickness: a 10-fold reduction in film thickness is accompanied by a 3-fold decrease in absorbed NMP*. This is evidence that the rate of diffusion of NMP through the film is relatively rapid, though not sufficient to produce a completely uniform distribution within 15 min. After 60 min of storage in the NMP*-doped airstream, the NMP content of films of resist A is proportional to film thickness (Figure 11), indicating that at that elapsed time the NMP depth distribution is largely uniform.

NMP uptake by resist B shows a different response to film thickness variation than that exhibited by resist A. Figure 11 shows the NMP incorporation by resist B is essentially independent of film thickness. This implies that under these conditions all the absorbed NMP* is concentrated within the top 0.1 μm of the film. The lithographic response of resist B to NMP contamination is consistent with accumulation of NMP near the top surface of the film. This resist can be imaged in positive tone with deep-UV light at a dose of approximately 2.5 mJ/cm^2. Figure 12 shows the effect of airborne NMP contamination on the imaging properties of resist B. The left photomicrograph in Figure 12 displays the final developed image obtained when the resist film is stored in uncontaminated filtered air for 15 min after coating and prior to expose, postexposure bake, and develop. The right-hand photomicrograph shows the effects of storing an identical film in an atmosphere of filtered air containing 10 ppb NMP for 15 min after coating. The formation of a thin, poorly soluble "skin" at the air–resist interface is evident. The skin is $\sim$0.1 μm thick, consistent with the measured depth distribution of NMP in B.

Though the amount of NMP absorbed by resist B under these conditions is small, the amount of photogenerated acid in the film is also quite low. Furthermore, successful imaging of resists containing *t*-BOC–styrene require very strong acid. This implies that any reduction in acid strength (due to protonation of an impurtiy) will have a major effect. Assisted by other published work, it is possible to make an order-of-magnitude comparison between the amount of photogenerated acid produced in these resists and the amount of absorbed NMP found in this study. McKean et al. have reported direct determination of the photoacid generated in PBOCST containing Ph_3SSbF_6, using a merocyanine dye technique.[23] Chemical interferences prevent the use of their technique to measure the photoacid in resist B, but in view of the similarity in composition and chemistry, it is expected that the published PBOCST results provide an adequate approximation of the photoacid produced in B. Using the PBOCST results as a guide, we estimate that a deep-UV flood exposure at a 2.5 mJ/cm^2 dose produces 170 nmol of $HSbF_6$ in a 1.0-μm-thick × 125-mm diameter film of B. Assuming for simplicity a uniform depth distribution of acid, the top 0.1-μm-thick layer of the film then contains 17 nmol of $HSbF_6$. The data in Figure 11 show that the resist film has absorbed about 6 nmol of NMP. This estimate demonstrates that the amount of absorbed NMP, though low, is of the same magnitude as the amounts of photogenerated acid present in these systems. Referring to tabulated pK_a values,[24] NMP is strongly basic compared to the other functional groups present in the resist and would therefore be expected to react with the photogenerated acid, in this case neutralizing about one-third of the acid in the top 0.1 μm of the film.

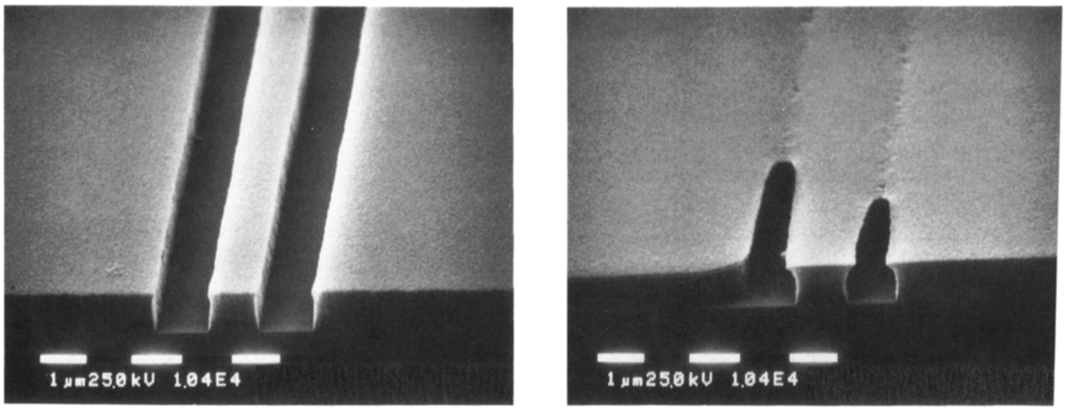
Influence of Resist Composition on NMP Uptake Rates. As discussed earlier in this paper, one can protect acid-catalyzed chemically amplified resist films from airborne chemical contamination by working in a carbon filtered environment or by overcoating the resist film with a protective barrier layer. However, neither of these meth-

---

(22) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: Oxford, 1975; pp 254–255.

(23) McKean, D.; Schaedeli, U.; MacDonald, S. Bronsted Acid Generation from Triphenylsulfonium Salts in Acid-Catalyzed Photoresist Films. In *Polymers in Microlithography: Materials and Processes*; ACS Symposium Series No. 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington, D.C., 1989; 27–38.

(24) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley and Sons: New York, 1985; pp 220–222.



15 min in filtered air

15 min in 10 ppb NMP before exposure

Figure 12. Lithographic effect of resist B contaminated with 10 ppb of NMP.

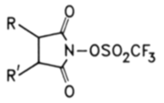
ACID GENERATOR ADDED TO FILM	AMOUNT NMP ABSORBED IN 15 MIN (ng/wafer)
None	689
Ph_3S-SbF_6	583
	570

Figure 13. Effect of photoacid generator on NMP absorption by resist B.

POLYMER	AMOUNT NMP ABSORBED IN 15 MIN (ng/wafer)
poly(styrene)	64
poly(4–hydroxystyrene)	758
poly(4–methoxystyrene)	135
poly(4–t–BOC–styrene)	547
poly(methylmethacrylate)	70
m–cresol novolac	164
epoxy–cresol novolac	18

Figure 14. Effect of polymer structure on NMP absorption.

ods would be required if the resist film simply did not absorb contaminants from the air. With this in mind, we have used our radiochemical method to examine the degree to which resist film composition influences NMP uptake. The two composition variables we examined were photoacid generator and resin structure.

The addition of photoacid generators appears to only weakly influence NMP uptake properties. The table in Figure 13 summarizes results obtained when the composition of resist B was modified. This table lists the amounts of NMP* absorbed in 15 min from the NMP*-doped airstream. Note that neither ionic photoacid-generators (PAGs) (a sulfonium salt added at 5 wt %), nor nonionic PAGs (an imido triflate[25] added at 8 wt %) causes a significant change in NMP uptake, as compared to pure polymer films.

In contrast, the polymer structure *strongly* influences the degree of NMP uptake. The table in Figure 14 lists amounts of NMP* absorbed by various polymer films after 15 min in an NMP*-doped airstream. NMP* contents vary by a factor of 40 in this list. An examination of these data suggests that the relation between NMP uptake and polymer structure is a complex one. For example, comparison of the data on poly(styrene) and poly(hydroxystyrene) implies that the presence of hydroxyl groups enhances the rate of NMP uptake. However, poly(*t*-BOC–styrene), which contains no hydroxyl groups, absorbs NMP at a rate only slightly less than poly(hydroxystyrene), and at a rate much greater than cresol–novolac, which bears phenolic hydroxyl groups and is isomeric to poly(hydroxystyrene). While the factors controlling NMP uptake have not yet been identified, it is clear that the polymer structure profoundly influences NMP incorporation.

The data shown in Figure 14 should be encouraging to those research laboratories involved in designing new chemically amplified resist systems. These data show that one can alter the NMP absorption rate by changing the chemical structure of the resist resin. In particular, relatively minor deviations from PBOCST can result in a lower NMP absorption rate. This holds out the possibility of designing a new resist system with a low NMP absorption rate, which will not be affected by airborne chemical contamination.

Concluding Remarks

In this paper we have shown that the lithographic performance of an acid-catalyzed chemically amplified resist can be degraded by ppb levels of an organic base. Using ^{14}C labeled NMP (at 10 ppb concentration) we have demonstrated that resist films do absorb airborne contaminants, that the diffusion into the film is Fickian, and that the absolute amount of absorbed NMP at the resist surface is on the same scale as the amount of photogenerated acid. In view of these data, we believe that the degradation in image quality that occurs when PBOCST (or resist systems derived from *t*-BOC) films stand in "clean room air" is consistent with absorption of some basic airborne contaminant. This absorbed base can neutralize a portion of the photogenerated acid, effectively poisoning the catalyst required for the chemical amplification process. Work at AT&T Bell Laboratories supports this theory as Nalamasu et al. reached a similar conclusion

---

[25] Brunsvold, W.; Montgomery, W.; Hwang, B. Advances in Resist Technology and Processing VIII. *Proc. SPIE* **1991**, *1466*, 368–376.

regarding the degradation of apositive tone resist system (CAMP) that contains a *t*-BOC species.[16]

While we have demonstrated that ppb levels of an organic base can degrade the image quality of these resist systems, we have also demonstrated that these resists can be used in a semiconductor production environment, provided certain precautions are taken. Specifically, localized air filtration through activated carbon was used in the manufacture of 1 Mbit DRAM devices,[7] and a protective overcoat layer was used in a 16 Mbyte DRAM process.[9] More importantly, the realization that airborne organic bases can induce this imaging problem paves the way toward its resolution. We have discussed two broadly applicable engineering solutions to the problem that are now at hand: (1) removal of contaminants by high efficiency chemical filtration, and (2) application of an overcoat or barrier layer to protect the resist. Longer term, a more satisfying solution is to devise new chemically amplified resists specifically designed to be insensitive to airborne basic contaminants. The work described in this paper suggests this goal can be achieved in several ways: (1) by selecting or designing a polymer which has a low permeability to organic contaminants; (2) by designing systems which have short catalytic chain lengths (while this may reduce photospeed, it should also reduce the impact of acid neutralization via contamination); (3) by selecting an acid-labile functional group that is a relatively strong base to enable the functional group to compete effectively against basic impurities for the photogenerated acid. Hopefully, the next generation of acid catalyzed chemically amplified resists will exhibit increased process latitude by incorporating one or more of these concepts.

Acknowledgment. We thank C. J. Knors and N. B. Deyoe (IBM E. Fishkill) for the data in Figures 7 and 8 and H. Ito (IBM Almaden Research Center) for use of the photomicrographs in Figure 12. We also thank the dedicated processing engineers of IBM Burlington and IBM E. Fishkill who implemented these chemically amplified DUV resists on the manufacturing floor.