Quantitation of Airborne Chemical Contamination of Chemically Amplified Resists using Radiochemical Analysis

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ABSTRACT

Many chemically amplified resists based on acid catalysis exhibit extreme sensitivity to trace quantities of airborne organic contaminants. This sensitivity is manifested as a rapid degradation in lithographic properties upon standing in clean room air. In this work we have studied the absorption of one such airborne contaminant, N-methylpyrollidone (NMP), by thin polymer films. NMP labeled with radioactive ^{14}C was introduced at a concentration of 10 ppb into a stream of purified air, and the film of interest was immersed in that airstream for a predetermined time under controlled conditions. This method provides an ideal means for determining rates of NMP uptake, correlating resist lithographic performance with absorbed NMP content, and for examining the effects of film thickness and composition on rates of absorption.

1. INTRODUCTION

The interest in resist materials based on chemical amplification (CA) is high and increasing throughout the microelectronics industry.[1] This class of resists functions by combining the radiation-induced production of a small quantity of a catalyzing acidic species with thermally activated chemistry designed to produce a change in film solubility or some other property upon action by the catalyst. The use of one such chemically amplified DUV resist in the manufacture of 1 Mbit DRAM has been described.[2]

While such resists exhibit very high photosensitivities due to the gain inherent in the imaging chemistry, it has been demonstrated that the presence of very low levels of certain organic vapors in the ambient environment can severely degrade their performance. For example, airborne N,N-dimethylaniline has been shown to sharply decrease the radiation sensitivity of TBOC resist even when present at levels well below one hundred parts-per-billion.[3] 1-Methyl-2-pyrollidone (N-methylpyrollidone or NMP), widely used for casting and stripping of organic films in microelectronics fabrication, has been identified as another substance capable of causing degradation of CA resists.[4]

This report summarizes our study of NMP absorption by a series of thin resist and polymer films immersed in an airstream containing extremely low concentrations of NMP vapor. Radiolabeled 1-[^{14}C]-methyl-2-pyrollidone (NMP*) was added as a tracer to allow determination of absolute amounts of absorbed NMP. A series of experiments designed to quantify amounts of contaminant

absorbed by resist films, to determine the kinetics of NMP uptake, and to characterize the effects of film thickness and composition are described.

2. EXPERIMENTAL

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

The experimental apparatus is shown schematically in Figure 1. It is based on the design of MacDonald et al.[3] 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 ft³/min. The airstream is split in half at a tee-fitting downstream from the filter. A low flow of NMP*-laden nitrogen (~ 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 foot 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. In the experiments described here, the final concentration of NMP* in the doped airstream was 10 ppb.
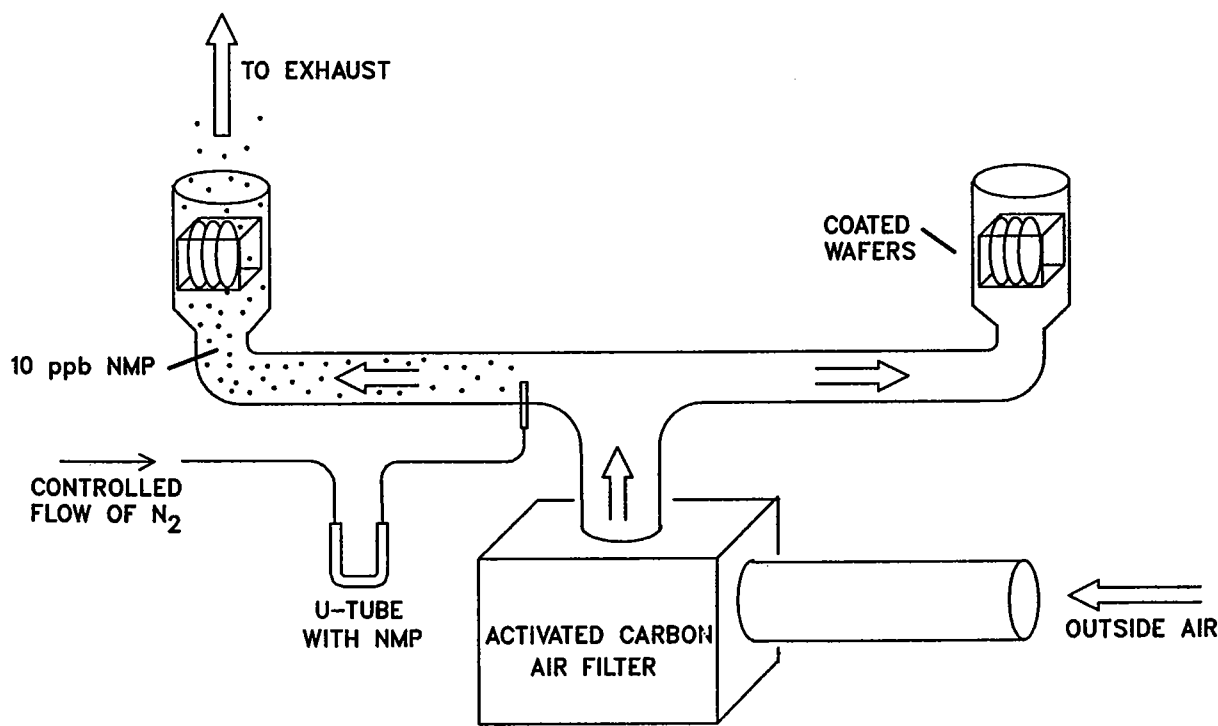

FIGURE 1: Experimental apparatus used in this study.

Radiolabeled 1-[14C]-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 x 10^6 dpm/mg.

The experimental protocol was as follows. After allowing the air-handling apparatus to operate for at least 30 minutes to stabilize, a series of coated wafers was prepared and placed in the NMP*-laden airstream. After a timed period the wafers were withdrawn. With each wafer the coating was stripped with 5 mL of an appropriate solvent (typically propylene glycol monomethyl ether acetate), followed by twice rinsing the wafer and stripping vessel with aliquots of Aquassure LSC cocktail (NEN, Dupont). The level of ^{14}C activity in the combined stripping liquids was then measured by liquid scintillation counting. Throughout this study duplicate measurements were always carried out. In general, for all materials studied, the difference between duplicate samples within a run was less than 10%.

3. RESULTS AND DISCUSSION

3.1 Rates of NMP Uptake

Figure 2 displays the amounts of NMP* absorbed onto coated and uncoated silicon wafers as a function of time in the NMP*-doped airstream. The amount adsorbed to bare silicon is small and is essentially constant over a 30 minute time period. Application of a one micron film of TBOC resist containing Ph$_3$SSbF$_6$ to the silicon substrate leads to a sharp increase in the rate of NMP uptake.
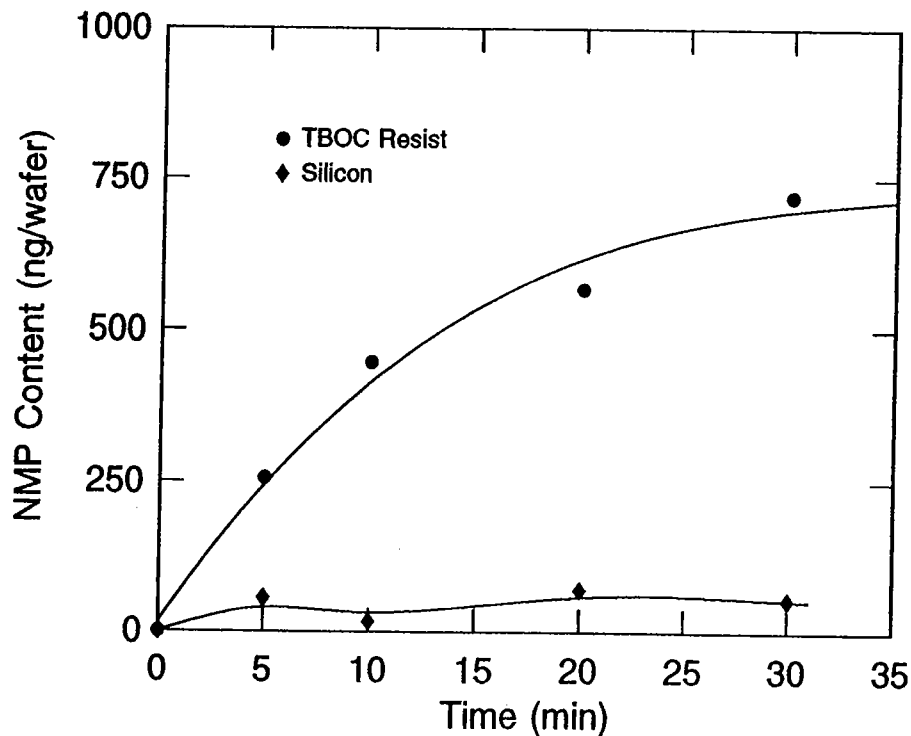

FIGURE 2: Absorbed NMP versus Time in NMP-doped Airstream for TBOC Resist.
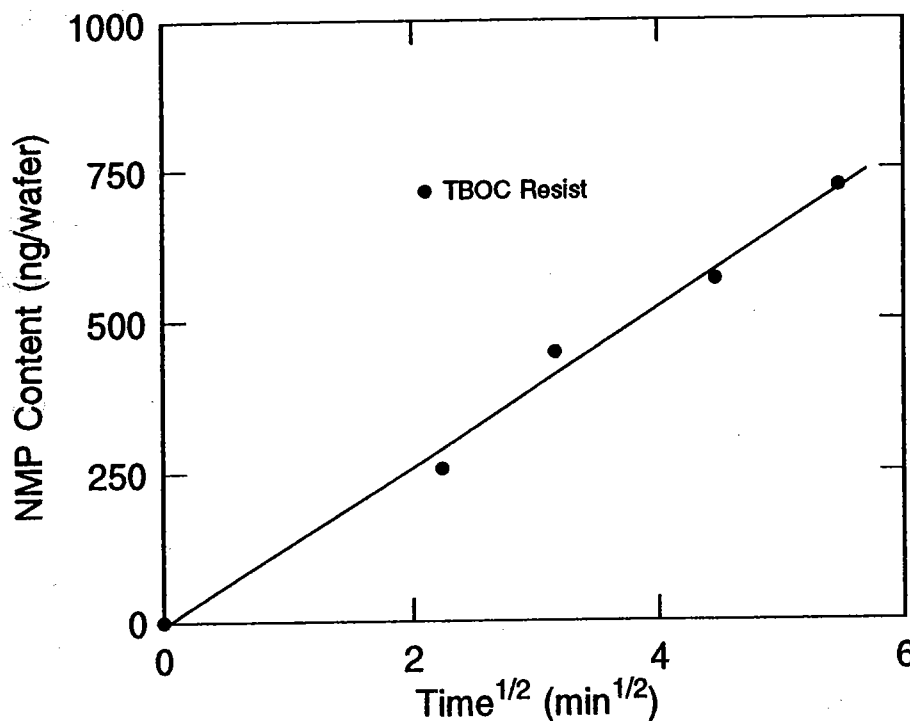
FIGURE 3: Absorbed NMP versus (Time)$^{1/2}$ for TBOC Resist.

After 10 minutes, a bare silicon wafer has adsorbed 20 ng NMP* while the TBOC-coated wafer has absorbed 450 ng NMP*. This amount, corresponding to about 30 parts NMP per million parts of polymer on the wafer, is sufficient to cause noticeable degradation in resist properties: lithographic evaluation of TBOC resist shows significant linewidth shifts (~0.3 μm shift in a 1.0 μm feature) after 10 minutes in an airstream containing 10 ppb NMP.

From Figure 2, the total amount of NMP* absorbed by a TBOC 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 expectation is that the diffusion process is Fickian.[5] If Fickian diffusion kinetics apply, then the total amount absorbed should increase linearly with the square root of elapsed time.[6] Figure 3 shows the TBOC data of Figure 2 plotted in this manner. The relationship is linear within the precision of the experiment.

3.2 Depth Distribution of NMP in the Polymer Film.

Characterization of the depth distribution of NMP in resist films may aid in understanding how airborne contamination affects lithographic imaging. Several distinct depth distributions are possible:

1. a uniform distribution, i.e., one wherein the NMP concentration is the same throughout the film. This will occur if diffusion of NMP through the film is relatively fast on the time scale of the experiment;

2. the case 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; and

3. a depth distribution of NMP that is somewhere between these two extremes.

One way to characterize the NMP depth distribution is to determine how the amount of absorbed NMP varies as the thickness of applied polymer film is decreased. If the NMP content decreases in proportion to the film thickness, then the depth distribution is uniform. If the NMP content is independent of the film thickness, then the absorbed material is concentrated near the interface. NMP depth distributions were examined in this manner for two resist systems:

(A) an experimental positive-tone CA resist composed of a copolymer incorporating the t-BOC-styrene monomer and 5 weight percent Ph_3SSbF_6; and

(B) standard TBOC resist which contains poly(t-BOC-styrene) and 5 weight percent Ph_3SSbF_6.

For each resist, films of 1.0 μm and 0.1 μm thickness were placed in the NMP*-doped airstream for 15 minutes. The amounts of NMP* absorbed by each film are given in the table in Figure 4. NMP uptake by resist A 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. For resist B the amount of absorbed NMP* *is* a function of thickness : a 10-fold reduction in film thickness is accompanied by a three-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 minutes. After 60 minutes storage in the NMP*-doped airstream, the NMP content of films of resist B is proportional to film thickness (Figure 4), indicating that at that elapsed time the NMP depth distribution is largely uniform.

RESIST A

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

RESIST B

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

FIGURE 4: Absorbed NMP versus Film Thickness for Resists A and B.

The lithographic response of resist **A** 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 5 shows the effect of airborne NMP contamination on the imaging properties of resist **A**. The left photomicrograph in Figure 5 displays the final developed image obtained when the resist film is stored in uncontaminated filtered air for 15 minutes after coating and prior to expose, post-expose 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 minutes after coating. The formation of a thin, poorly soluble "skin" at the air-resist interface is evident. The skin is ~ 0.1 μm thick, consistent with the measured depth distribution of NMP in **A**.

Though the amount of NMP absorbed by resist **A** under these conditions is small, the amount of photogenerated acid in the film is also quite low. An order-of-magnitude comparison of these two quantities is possible. McKean et al. have reported direct determination of the photoacid generated in poly(t-BOC-styrene) containing Ph_3SSbF_6, using a merocyanine dye technique.[7] Chemical interferences prevent the use of their technique to measure the photoacid in resist **A**, but in view of the similarity in composition and chemistry, it is expected that the published TBOC results provide an adequate approximation of the photoacid content in **A**. Using the TBOC results as a guide, we estimate that a deep-UV flood exposure at a 2.5 mJ/cm^2 dose produces 170 nmole $HSbF_6$ in a 1.0 μm-thick x 5 inch-diameter film of **A**. Assuming for simplicity a uniform depth distribution of acid, the top 0.1 μm-thick layer of the film then contains 17 nmol of $HSbF_6$ and about 6 nmol NMP (calculated from the data of Figure 4). 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,[8] 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.
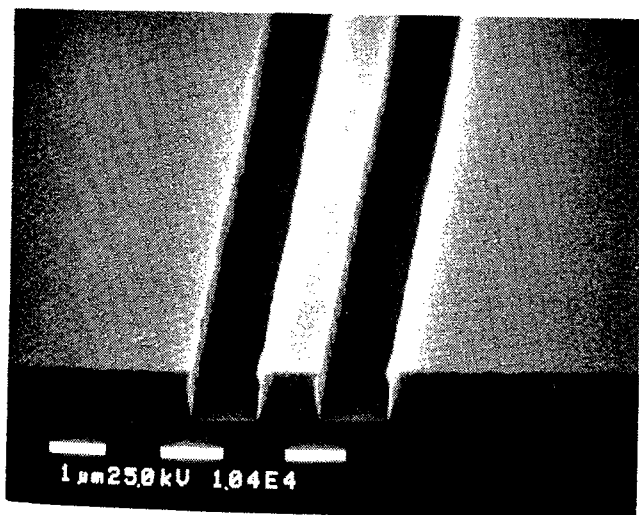
15 min in filtered air
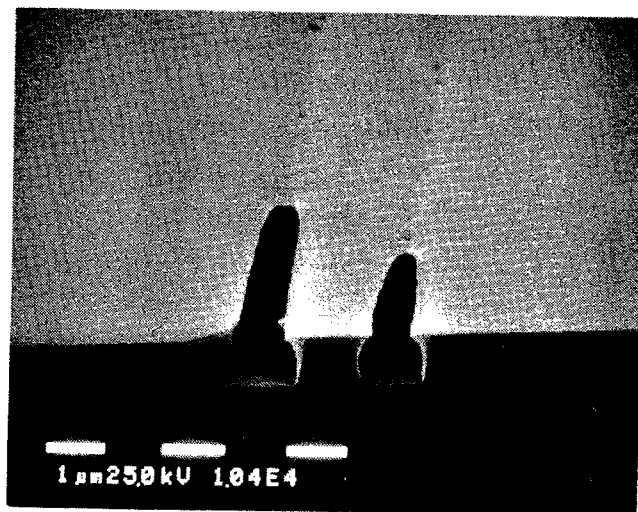
15 min in 10ppb
NMP before exposure

FIGURE 5: Lithographic Effects of NMP Contamination of Resist **A**.

3.3 Influence of Resist Composition on NMP Uptake Rates

Since the effects of airborne contamination on CA resist performance were first identified, several methods for controlling environmentally-induced aging have been proposed. In one scheme, the wafer is maintained in a purified atmosphere at critical stages of the lithographic process.[3] An alternate approach is the application of a protective barrier coating over the resist film to shield against environmental contaminants.[9] There is evidence that resist composition can also influence susceptibility to airborne contamination effects. For example, it has been reported that a deep-UV resist based on hexamethoxymelamine exhibits no linewidth shift even with delays as long as 23 hours.[10]

If the absorption of airborne basic substances by a resist film can be minimized, then it is expected that their effects on the resist's lithographic properties will also be minimized : the lower the contaminant uptake, the more stable will be the resist properties. With this in mind, we have used our radiochemical method to examine the degree to which the composition of a resist film influences NMP uptake. The two composition variables we examined were photoacid generator and resin structure. Our preliminary study suggests that there is potentially much leverage in optimizing the resist chemistry to minimize contaminant absorption.

The addition of photoacid generators appears to only weakly influence NMP uptake properties. The table in Figure 6 summarizes results obtained when the composition of resist A was modified. It lists the amounts of NMP* absorbed in 15 minutes from the NMP*-doped airstream. Neither ionic PAG's (a sulfonium salt added at 5 weight percent) nor nonionic PAG's (an imido-triflate[11] added at 8 weight percent) cause a significant change in NMP uptake compared to films of the pure polymer.

In contrast, the polymer structure *strongly* influences the degree of NMP uptake. The table in Figure 7 lists amounts of NMP* absorbed by various polymer films after 15 minutes in an
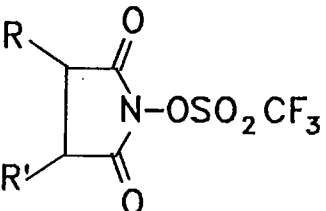
Acid Generator	NMP Content (ng/wafer)
none	689
$Ph_3S\ SbF_6$	583
	570

FIGURE 6: Effect of Photoacid Generator on NMP Absorption by Resist A.

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.

4. CONCLUSIONS

We have described a method for the direct quantitation of a typical airborne contaminant, N-methylpyrrolidone, absorbed into thin polymer films. Using this method it can been shown that, for TBOC resist, the absorption of NMP exhibits kinetics consistent with a Fickian diffusion process. Depending on the resist composition, the absorbed NMP can be concentrated in a region of the polymer film near the air interface, or can be more uniformly distributed through the film. We have obtained data which indicates that the addition of either ionic sulfonium salt photoacid generators or nonionic photoacid generators does not significantly change the rate of NMP uptake of a typical photoresist film. In contrast, by varying polymer structure the rate of NMP uptake can be modified by large factors.

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 7: Effect of Polymer Structure on NMP Absorption

5. ACKNOWLEDGMENTS

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