Airborne Contamination of a Chemically Amplified Resist. 2. Effect of Polymer Film Properties on Contamination Rate

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Many chemically amplified resists exhibit severe degradation of lithographic properties upon exposure to very low concentrations of organic base vapor. Measured rates of absorption of such contaminants by thin resist and polymer films vary over a wide range depending on the chemical structure of the polymer comprising the film. We describe here a study aimed at identifying those film characteristics that significantly influence contaminant uptake rates. We test whether the kinetics of contaminant absorption are controlled by (1) the amount of residual casting solvent in the film and/or (2) the physical properties of the polymer comprising the film. Radiotracer techniques are used to quantify casting solvent residue in thin polymer films and to characterize the kinetics of absorption by such films of *N*-methylpyrrolidone, a common airborne contaminant. The results of this study provide guidance in the design of chemically amplified resists resistant to airborne chemical contamination.

Introduction

Resist systems based on acid-catalyzed chemical amplification (CA) can exhibit very high radiation sensitivity, but this is accompanied in most cases by an extreme susceptibility to adventitious basic airborne contaminants. In the first paper of this series, we reported that airborne amines and *N*-methylpyrrolidone (NMP) cause image degradation characterized by line-width shifts and, in the case of positive-tone CA resists, by formation of a thin, poorly-soluble "skin" on the resist film, even at extremely low vapor concentrations on the order of 15 ppb.[1] This problem of catalyst poisoning by airborne organic base is a major issue for acid-catalyzed resist systems, and in general, the practical application of positive tone CA resists at present calls for extraordinary measures to protect the films against such contamination.[2-5] The design of environmentally robust CA resists that exhibit high photospeed and contrast without special handling or processing is an important goal and a significant challenge. An improved understanding of factors that influence resist susceptibility to environmental contamination would simplify the search for improved materials.

If one assumes that an absorbed contaminant degrades resist performance by simple acid-base neutralization of the photogenerated catalytic species, then the degree of degradation should be related to the relative basicities of the contaminating species versus the resist components, the catalytic chain length, and the rate at which the contaminant enters the resist film. Figure 1 schematically describes the contamination effect for *t*-BOC resist system as a competition between the desired acid-catalyzed deprotection chemistry and the interfering acid/base-contaminant reaction. Minimization of the contamination effect can be effected in several ways: (1) By increasing the basicity of functional groups in the resist, which allows their more effective competition for the photogenerated catalytic acid. In general this limits the types of deprotection chemistry which can be utilized in such resists. (2) By increasing the acid concentration formed upon exposure such that the expected level of contamination does not neutralize a significant fraction of the photoacid. The drawback here is that an increase in acid production will translate to an increased exposure dose requirement. (3) By designing the resist material/process such that basic contaminants are excluded from the resist film.

Two approaches for exclusion of contaminants from CA resist films have been reported. In the first, an overcoat[3,5,6] is applied to the resist film as a protective barrier layer. In the second, the resist film is stored in a purified atmosphere during all critical stages of the lithographic process.[1,2] Both techniques add complexity and cost to the resist processing. In the preferred solution, the CA resist chemistry/process would incorporate an intrinsic, self-contained means of excluding airborne contaminants.

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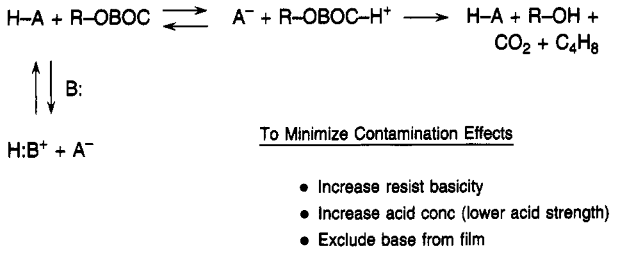

Figure 1. Schematic diagram of the chemically amplification process in TBOC-Sb resist.

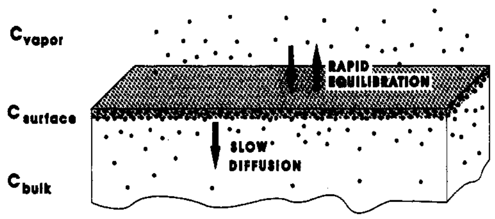

Figure 2. Schematic diagram of polymer permeation by a vapor using the solution-diffusion model of permeation.

In the preceding paper in this series,[1] we reported that the rate of uptake of NMP by polymer films varies over a wide range as the chemical structure of the polymer comprising the film is varied. No simple relation linking polymer structure and NMP uptake was evident in those data. However, that observation suggests that it should prove possible, by appropriate selection of materials, to design CA resist materials with decreased sensitivity to airborne basic contamination. Our goal in this study is to correlate these observed differences in contaminant uptake with properties of the different polymer films.

Polymer Permeation

The problem of acid-catalyzed CA resist films absorbing organic base vapor is another example of the more general issue of polymer permeability. Fortunately, the permeability of polymer films to vapors and gases has been studied in great detail over the past several decades.[7,8] Permeability is an important consideration in such diverse fields as food storage, membrane separations, and electronic packaging. The permeation process in films is generally treated in terms of the solution diffusion model, in which the permeant first sorbs onto the surface of the film and then diffuses through the polymer. Figure 2 is a schematic representation of this model. Initially, a rapid equilibration occurs between the permeant vapor and the surface of the polymer film. The surface concentration will be governed by a Henry's law relation:

$$C_{\text{surface}} = SC_{\text{vapor}}$$

where C_{surface} is the surface concentration of permeant, C_{vapor} is the concentration of permeant in the vapor in contact with the surface, and the proportionality constant S, termed the *solubility* of the permeant in the film, is constant for a given polymer/permeant pair at constant temperature. This initial equilibration is followed by slow diffusion of permeant from the surface layer into the bulk film under influence of the concentration gradient formed by the surface layer. Since the uptake of airborne contaminants (such as NMP) in resist films has been shown to have behavior characteristic of a Fickian process,[1] the diffusion can be described by Fick's law:

$$R = -D\,dC/dx$$

where R is the rate of diffusion, dC/dx is the concentration gradient, and D is the diffusion coefficient which is constant for a given polymer/permeant pair at constant temperature. From Figure 2 it is clear that the concentration gradient dC/dx is determined in part by the surface concentration C_{surface}. Thus the overall permeation rate P will be controlled both by the *solubility* of that substance in the film (a thermodynamic measure of the affinities of the permeant and polymer for one another) and by the *diffusivity* of the species through the film (a kinetic parameter measuring the mobility of permeant in the film):

$$P = f(\text{solubility},\text{diffusivity})$$

We will use the framework of this general permeation model to assess the results of the present study on spin-coated films. Factors controlling permeability include permeant size, shape, and structure, polymer composition and free volume, and the mobility of polymer segments.

We know from past work that the amount of residual casting solvent in thin polymer films varies over a wide range depending on the characteristics of the polymer and the solvent. From the preceding discussion, the rate of permeant uptake by a film is determined in part by the ease with which the permeant diffuses in the film. Therefore, one possible cause of the variation in contaminant uptake among the different polymers is that they contain differing levels of residual casting solvent. In this work we examine this possibility by measuring the residual solvent content of eight spin-coated films along with their propensities to absorb NMP vapor.

If the chemical structure of a film changes, the physical properties of a film cast from that polymer will vary accordingly, and these changes are expected to influence permeability. In this work we address these issues by measuring the NMP vapor uptake for 24 polymer films and examining the relationship between NMP incorporation and specific polymer properties.

Experimental Section

Synthesis of Carboxyl-^{14}C-Propylene Glycol Monomethyl Ether Acetate (PGMEA*). Carboxyl-^{14}C-acetyl chloride (California Bionuclear Corp., 2.0 mCi, specific activity 1.8 mCi/mmol) was dissolved in 10.0 mL of pentane containing acetyl chloride (918 mg, 11.7 mmol). The total was transferred to a 50-mL round-bottom flask previously purged with dry nitrogen. 1-Methoxy-2-propanol (901 mg, 10.0 mmol) was added to the reaction. The flask was immersed in an ice bath and triethylamine (1265 mg, 12.6 mmol) was added dropwise with vigorous magnetic stirring. After complete addition, the reaction was allowed to warm to room temperature and stand for 1 h. The reaction was worked up by treating sequentially with water (1.3 mL), saturated NaH_2PO_4 in water (2 mL), and saturated $NaHCO_3$ in water (2 mL). The hydrocarbon phase was pressure-filtered through a pad of anhydrous magnesium sulfate; additional pentane was added to transfer the solution and wash the drying agent. The filtrate was gently distilled to remove most of the pentane and then transferred to a microdistillation apparatus. The product was distilled at 150 °C. Although not weighed, previous nonradioactive runs gave a yield of about 70% (ca. 1000 mg). In this case, additional portions of nonlabeled PGMEA (2 × 1 g) were added to the pot residue and distilled into the labeled product producing an approximate total yield of 3 g. The resulting

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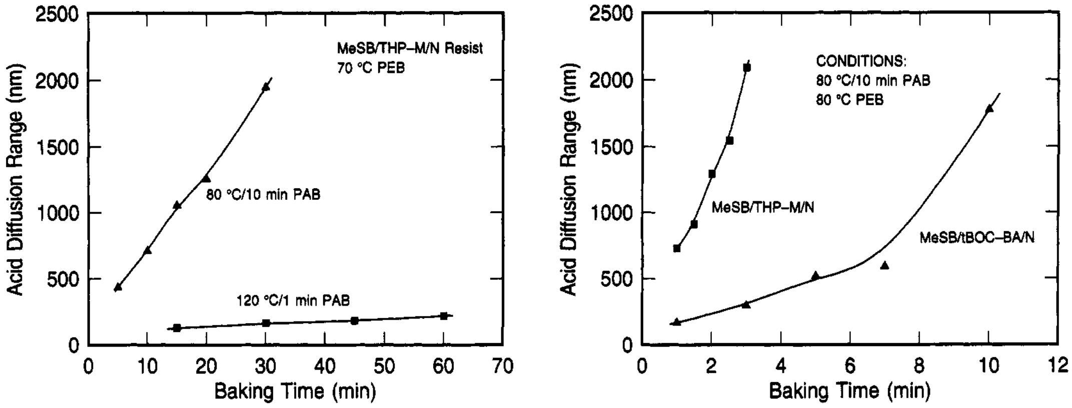

Figure 3. Influence of (a, left) postapply bake temperature and (b, right) polymer structure on acid diffusion range. These data are taken from ref 11.

colorless liquid was characterized by gas chromatography (stationary phase = OV 225). Purity was estimated at 98.7%, the only other volatile material being pentane. Specifically, neither acetic acid nor triethylamine was detected. The specific activity of the product was 57.7 μCi/mmol.

Quantitation of Residual Casting Solvent. A radiochemical method was used to determine film solvent content after a typical spin-coat/postapply bake cycle. A series of polymer solutions was prepared by combining an aliquot of PGMEA* with a solution of the polymer in unlabeled PGMEA. The final solutions had specific activities of ca. 5 μCi/mmol PGMEA. These solutions were applied as ca. 1-μm-thick films to tared 25-mm-diameter silicon wafers (weighed to ±0.01 mg) and postapply baked on a hotplate at 100 °C for 300 s. After a final weighing the films were stripped with 5 mL of unlabeled PGMEA and rinsed twice with Scintiverse II liquid scintillation cocktail (LSC, Fisher Scientific). The combined washings were assayed for ^{14}C using a Packard Tri-Carb 460 liquid scintillation system. All analyses were performed in duplicate; results from duplicate runs generally agreed within 5% and at worst within 10% of their average value.

Quantitation of NMP Uptake. The construction and use of the apparatus employed for this measurement have been previously described.[1] In the present work the airborne substance was methyl-^{14}C-*N*-methylpyrrolidone, obtained from Sigma Chemicals as a solution in hexane. After transfer of this solution to a U-tube, the hexane was evaporated in a nitrogen stream, and unlabeled NMP was added to provide a final specific activity measured to be 2.71×10^6 dpm/mg. Vapor from this sample of NMP* was mixed into the purified airstream to a final concentration of 12–15 ppb. Unless otherwise noted, the experimental protocol was as follows: After allowing the air-handling apparatus to operate for at least 30 min to stabilize, a series of coated wafers was prepared and placed in the NMP*-laden airstream. After a predetermined time period the wafers were withdrawn. For each wafer the coating was immediately stripped with 5 mL of an appropriate solvent (typically propylene glycol monomethyl ether acetate or, alternately, the initial casting solvent), followed by twice rinsing the wafer and stripping vessel with aliquots of liquid scintillation cocktail (Aquassure LSC, New England Nuclear (duPont), or Scintiverse II LSC (Fisher Scientific)). The combined washings were assayed for ^{14}C using a Packard Tri-Carb 460 liquid scintillation system. Results on duplicate wafers typically agreed within 10%.

To correlate residual solvent content and NMP uptake, a series of polymer solutions identical to those prepared for the solvent residue determination but containing only unlabeled PGMEA were applied as ca. 1-μm films to 125-mm-diameter silicon wafers, postapply baked on a hotplate at 100 °C for 300 s, and placed in an airstream containing 15 ppb NMP* for 60 min. In the correlation of polymer properties with NMP uptake, solutions of the polymers in appropriate casting solvents were applied as ca. 1-μm films to 125-mm-diameter silicon wafers, postapply baked on a hotplate at 100 °C for 300 s, and placed in an airstream containing 12 ppb NMP* for 15 min.

Results and Discussion

Influence of Residual Solvent on Diffusion. It is well accepted that the mobility of small molecules in polymeric materials can be strongly affected by the concentration of solvent in the polymer matrix.[9] Presumably the solvent promotes segmental motion by disrupting interactions between polymer chains, thereby enhancing diffusion within the matrix. Reports from other workers have described effects of residual solvent on diffusion in lithographic materials. In one study, significant differences in image profiles were observed with one CA deep-UV resist depending on the choice of casting solvent.[10] Of particular note was the appearance of a poorly soluble surface skin when the resist film was cast from diglyme. This effect was attributed to the influence of residual solvent on acid diffusion within the film. Another group has provided more direct evidence that residual casting solvent influences mobility in chemically amplified resists.[11] Figure 3 shows data from their study. In Figure 3a is plotted the acid diffusion range in two resist films of identical composition which were postapply baked at different temperatures. The film baked at the higher temperature exhibits a much decreased diffusion range, attributed to a lower level of residual solvent. Figure 3b shows a similar result for resist films of different polymer composition which were postapply baked using identical conditions. The different compositions retain casting solvent to different degrees. Again the acid diffusion range is much lower in the film with less solvent residue.

In our prior NMP uptake study,[1] the polymer films were prepared by spin-casting from various solvents (diglyme, cyclohexanone, toluene, or propylene glycol monomethyl ether acetate (PGMEA), depending on solubility characteristics of the polymer). In the present work we selected for study a series of polymers of interest in microlithography and with widely varying structural characteristics, all of which are soluble in a single casting solvent (PGMEA). The methodology used here is first to accurately quantify residual casting solvent in films of this set of polymers and second to correlate the concentration of residual solvent with the uptake rate of NMP.

Table 1 summarizes the residual solvent contents for a series of polymer films of interest in microlithography,

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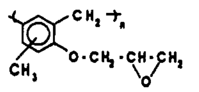
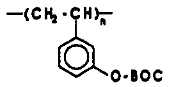
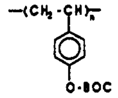
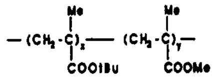
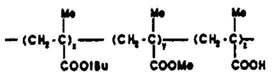
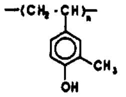
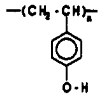
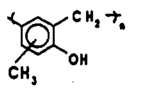
(11) Schlegel, L.; Ueno, T.; Hayashi, N.; Iwayanagi, T., *J. Vac. Sci. Technol.* **1991**, *9*, 278–289.

Table 1

polymer	structure	residual solvent (wt %)	NMP content[a] (ng/wafer)
epoxy–novolac		0.05	10
P(*m*-TBOCST)		0.5	120
P(*p*-TBOCST)		0.6	931
P(TBMA–MMA)		5.9	150
P(TBMA–MMA–MAA)		8.6	110
P(3-Me-4-HOST)		12.8	578
P(*p*-HOST)		20.4	1605
cresol–novolac		21.1	268

[a] After 60 min in 15 ppb NMP airstream.

tabulated on a weight percent basis. Depending on the properties of the polymer, residual solvent varies from 0.05 to 21 wt %. The general trend is that the level of solvent residue is related to the overall polarity of the polymer, with polymers of similar structure exhibiting nearly identical solvent levels. One noteworthy aspect of these data is that the amount of residual solvent can be substantial. In the case of the *m*-cresol–novolac film, about one-fifth of the film on a weight basis is retained solvent. We have found in further work on the cresol–novolac system that (1) the addition of 23 wt % of a typical 5-substituted diazonaphthoquinone (DNQ) to the novolac film does not significantly change its retention of PGMEA, (2) the solvent level does not decrease significantly with more extended bake times as long as 30 min, suggesting that the PGMEA is relatively strongly bound to the polymer, and (3) otherwise identical films formulated using ethyl cellosolve acetate as casting solvent retain similar proportions of solvent after baking. These observations demonstrate that residual casting solvent can be a major component of films of DNQ-novolac photoresists, though its presence and its role in influencing resist properties are often disregarded.

Our measurements suggest that the structure of the casting solvent has no significant influence on NMP uptake. A comparison of NMP absorption by polymer films cast from PGMEA with that of otherwise identical films cast from other solvents reveals similar rates of uptake. For example, 1.0-μm films of cresol–novolac (postapply baked as above) absorb 165 ng of NMP in 15 min when cast from a diglyme solution and 176 ng of NMP when cast from PGMEA solution. Analogous NMP uptake results were obtained for an epoxy–novolac film cast from cyclohexanone or from PGMEA.

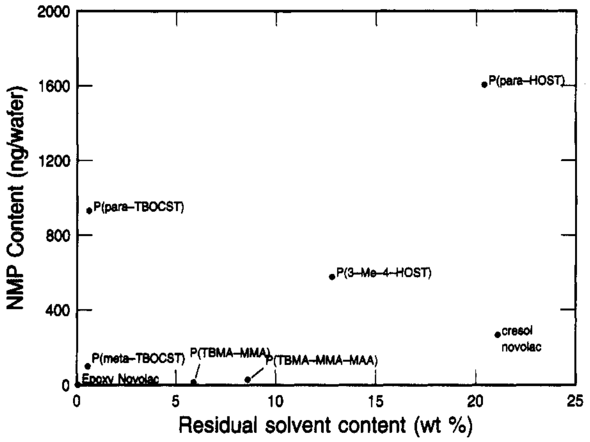


Figure 4. Plot of amount of NMP* absorbed in 1 h by a series of thin polymer films versus their residual casting solvent contents. In all cases the casting solvent used was PGMEA.

Figure 4 displays the relative absorption of NMP vapor for the polymer series shown in Table 1, plotted as a function of the residual (PGMEA) solvent content. No correlation between the solvent content of a film and its rate of NMP absorption is apparent. For example, the residual PGMEA content of P(*p*-TBOCST) is 1/35th that of the cresol novolac film, yet its rate of NMP uptake is about 3.5 times that of novolac. Similarly, compare the relative solvent contents and NMP absorption rates of P(*p*-TBOCST) and P(TBMA–MMA–MAA).

The films in this study were subjected to identical processing conditions, all were baked at 100 °C for 5 min. A close examination of the data of Figure 4 leads to the conclusion that polymer structural characteristics, rather

Table 2

polymer	NMP content[a] (ng/wafer)	solubility param ((cal/cm^3)$^{1/2}$)	T_g (°C)
poly(methyl methacrylate	70	9.1	115
poly(4-*t*-BOC–styrene)	547	9.5	135
poly(4-*t*-BOC–styrene) from Maruzen PHOST	400	9.5	115
m-cresol–novolac	164	13.0	100
poly(4-hydroxystyrene)	758	12.6	180
polystyrene	64	8.5	100
epoxycresol–novolac	18	10.0	39
poly(MMA–TBMA–MAA)	296	9.4	145
poly(α-Me-styrene-*co*-Bz-MA)	107	9.1	110
poly(tert-butylvinyl benzoate)	882	9.6	160
poly(3,5-Me_2-4-*t*-BOC-styrene)	362	9.9	130
poly(*tert*-butyl methacrylate)	25	8.3	118
poly(TBMA–MMA)	23	8.7	115
poly(3,5-Me_2-4-hydroxystyrene)	870	11.4	175
poly(α-Me-styrene) (low MW)	49	9.0	168
poly(α-Me-styrene) (high MW)	36	9.0	168
poly(acrylic acid)	36	14.4	106
poly(4-tert-butylstyrene)	315	9.0	145
poly(4-acetoxystyrene)	332	9.9	115
poly(methacrylic acid)	315	13.6	228
poly(4-MeO-styrene)	135	9.7	89
poly(4-MeO-styrene-*co*-4-*t*-BOC-styrene)	426	9.6	112
poly(3-*t*-BOC-styrene)	50	9.5	90
p(3-Me-4-hydroxystyrene)	340	11.3	135

[a] After 15 min in 12 ppb NMP airstream.

than the chemical nature of the monomeric repeat unit, are the dominant factors controlling contaminant absorption: (a) The residual PGMEA contents of films of P(*p*-HOST) and cresol–novolac are nearly identical. The chemical structural features of both polymers are quite similar (Table 1)—in fact the nominal repeat units are isomers. However their rates of NMP differ sharply, with the value for P(*p*-HOST) being 6 times that for cresol–novolac. (b) In an even closer comparison, the levels of solvent residue in P(*p*-TBOCST) and P(*m*-TBOCST) films are identical, and their chemical structures differ only in the position of substitution on the aromatic ring. However, their rates of NMP uptake differ by over a factor of 7.

Since the members of each of these pairs are so similar chemically, it would appear unlikely that the pronounced differences in NMP absorption stem from subtle changes in the chemical properties of the monomeric repeat unit. Clearly structure strongly influences NMP uptake. However, these results would suggest that the effect is an indirect one. In addition to altering the chemical properties, polymer structure can also influence such physical properties as polarity, molecular packing, and thermal properties.

Influence of Polymer Properties on Permeability. A total of 24 polymeric materials were characterized in this study. These were chosen so as to incorporate the widest practical range of functionality in the monomeric repeat unit. The materials set includes polymeric hydrocarbons such as poly(styrene) and alkyl-substituted derivatives, ethers (e.g., poly(methoxystyrene) and epoxy–novolac), carboxylic acids such as polyacrylic and poly(methacrylic) acids, aromatic and aliphatic esters (e.g., poly(acetoxystyrene), poly(*tert*-butylvinyl benzoate), poly(methyl methacrylate)), phenolic polymers, such as poly(hydroxystyrene) and alkyl-substituted derivatives, and copolymers incorporating combinations of the above functional groups.

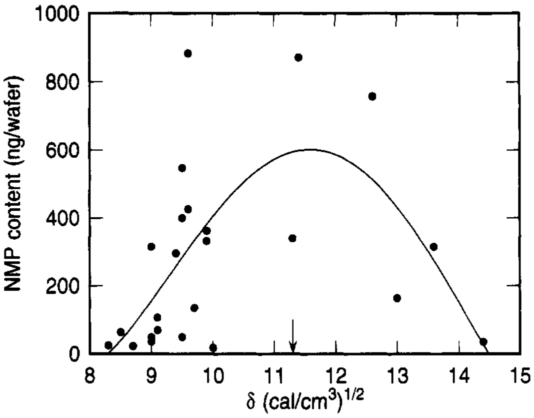


Figure 5. Amount of NMP* absorbed under equivalent conditions by various polymers as a function of the solubility parameter δ of the polymer. The solid line represents a fourth-order polynomial fit to the data.

Table 2 lists all polymers examined in this study, along with relevant physical properties and NMP incorporation data.

Effect of Solubility on NMP Uptake. Recall from the Introduction that the overall permeation rate of a substance into a polymer film is partially controlled by the solubility of that substance in the film. A useful methodology for quantifying the magnitude of the interaction between two substances is to determine the *solubility parameter* δ for both substances and to compare those values. The solubility parameter is rigorously defined in terms of the energies of interaction between molecules as measured by the heat of vaporization and includes contributions from dispersion forces, polar forces, and hydrogen bonding.[12] For our purposes, δ can be thought of as a measure of the polarity (or more precisely, the solvent power) of a substance. Materials with similar values of δ will be soluble in one another, and thus the method provides a means of quantifying the well-known rule-of-thumb that "like dissolves like".

For some of the polymers studied here, literature values of δ exist. In those cases where a direct measurement of δ was unavailable, its value was estimated using published methods based on group additivity.[13] The relation between NMP* uptake and δ for all materials examined in this study is shown graphically in Figure 5. The solid line in Figure 5 is a least-squares fit of a fourth-order polynomial to the data. The multiple-correlation coefficient[14] R characterizing the fit of the data to this line is 0.58. A value of $R = 1$ indicates a perfect correlation between data and the fitting function; a value of $R = 0$ indicates a complete lack of correlation. We take this value of R as an indicator that solubility is a factor influencing NMP absorption, even though the data show much scatter. The shape of the fitted line indicates that, among the materials set studied here, highly polar and highly nonpolar polymers do not absorb NMP as strongly as those of intermediate polarity. The maximum in the fitted curve occurs at a point approximately equal to the solubility parameter of NMP ($\delta = 11.2$).[13] The appearance of the curve is exactly analogous to those observed for equilibrium swelling of a

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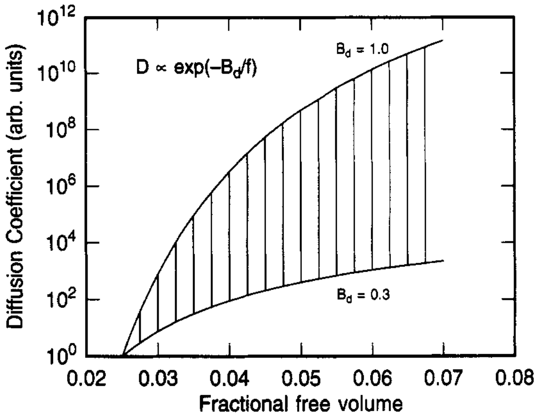

Figure 6. Relation between the diffusion coefficient for a permeant moving through a polymeric matrix and the free volume in the matrix.

polymer in solvents of differing δ.[15] These observations allow a tentative identification of polymer polarity as a significant parameter influencing the degree of NMP uptake. The scatter in the data suggests that other factors also play a role.

Effect of Free Volume on NMP Uptake. The presence of unoccupied, free volume in a polymer is considered to strongly influence the diffusivity of small molecules in polymers.[16,17] This is based on the assumption that a diffusing molecule can move from one place to another only when the local free volume around that molecule exceeds a certain critical value. The probability of finding such sufficient free volume will be related to the total free volume of the system. If the polymer possesses a high free volume due to inhibited chain packing, the permeability will be high. If the polymer possesses a low specific volume due to more efficient molecular packing (such as that resulting from crystallization, thermal annealing, or physical aging), then the permeability will be low. Relatively small changes in free volume may strongly influence the mobility of small molecules in a polymer matrix.[16] A theoretical analysis of the effect of free volume on diffusivity suggests that the diffusion coefficient D in this situation is described by the relation

$$D = Ce^{-B_d/f}$$

where C is a constant for a given polymer, permeant, and temperature, f is the fractional free volume, and B_d is a constant near unity.[17] Experimentally, values of B_d have fallen between 0.3 and 1.0 depending on the materials.[18-20] Figure 6 shows this relation in graphical form. Values of B_d between 0.3 and 1.0 will fall within the hatched region of the plot. Note that the vertical axis is logarithmic. The significant aspect of this plot is that a relativley small increase in free volume leads to large increase in D (the diffusion constant). For example, an increase in free volume from 2.5 to 4% leads to an increase in the value of D by 2–6 orders of magnitude.

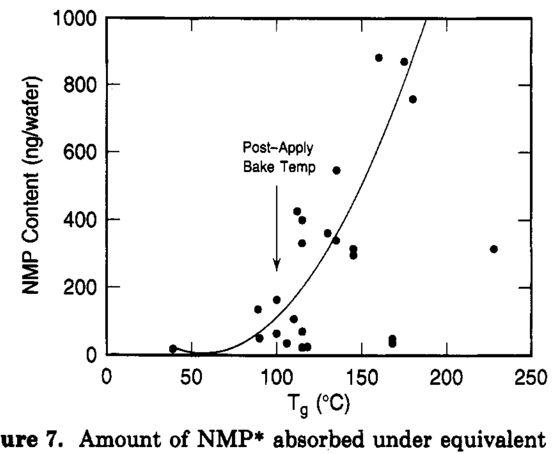

Figure 7. Amount of NMP* absorbed under equivalent conditions by various polymers as a function of glass transition temperature T_g of the polymer. The solid line represents a second-order polynomial fit to the data.

During the spin-coating process, large amounts of void or free volume are created in polymer thin films such as those used in photoresist formulations.[21] The amount of excess free volume can be reduced by heating near or above the T_g of the polymer. Pronounced differences in the properties of spin-coated polymer films following such thermal treatment have been attributed to changes in free volume.[21-23]

In the present study a range of polymer materials was examined with T_g values ranging from slightly above room temperature to over 200 °C. Figure 7 displays a plot of each film's NMP content after a 15-min exposure to 12 ppb NMP versus its T_g. It is clear from these data that a polymer's propensity to absorb NMP is strongly related to its T_g. Those materials with T_g values near or below 100 °C (the postapply bake used for all samples in this experiment) have absorbed essentially no NMP. The greater the margin by which a material's T_g exceeds the postapply bake temperature, the greater the amount of NMP it absorbs in a given time. This behavior is consistent with the presence of excess free volume generated by the spin-deposition process which enhances diffusion into the film. This excess free volume can be reduced (and correspondingly the diffusion rate will be reduced) by thermal annealing near or above the T_g of the material.

Those materials which deviate from this behavior are polymers which are at the extremes of the polarity scale: e.g., poly(α-methylstyrene), with a δ of 9.0 and a T_g of 168 °C, and poly(methacrylic acid), with a δ of 13.6 and a T_g of 228 °C. Apparently in these cases the polymers' affinities for NMP are so weak that there is little driving force for permeation to occur. If the NMP absorption data are plotted simultaneously againt both δ and T_g (Figure 8), then all data at hand can be accounted for with no anomalous outlying points.

The 3-D contour plot, shown in Figure 8b, is a very powerful way of analyzing the NMP uptake data. For

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(15) Reference 13, p 130, Figure 7.1.

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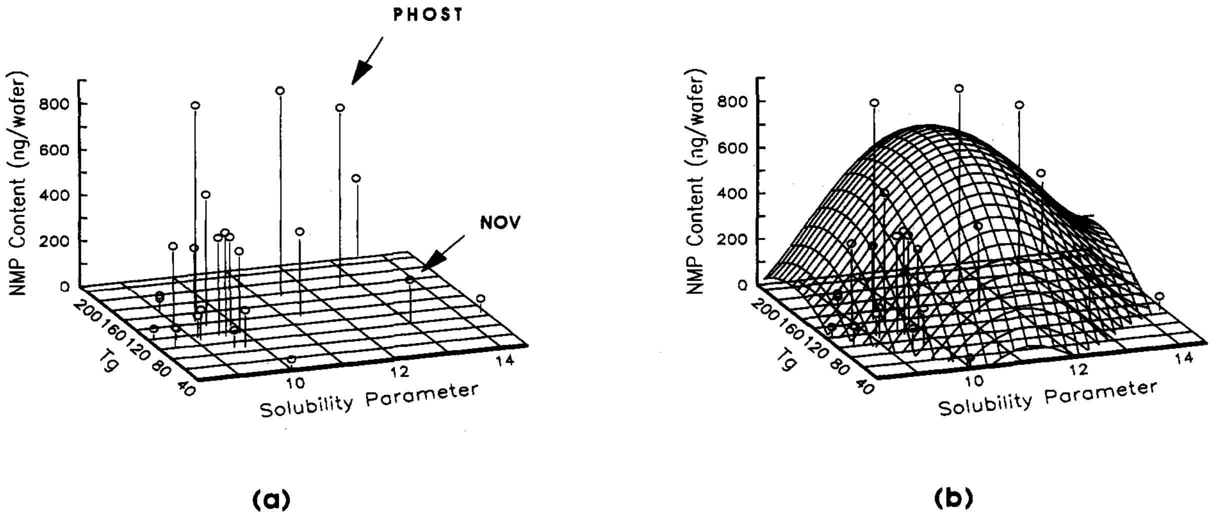

Figure 8. Amount of NMP* absorbed under equivalent conditions by various polymers as a function of both glass transition temperature T_g and solubility parameter δ of the polymer. The surface plotted in (b) is a polynomial least-squares fit to the experimental data.

example, consider the two films poly(*p*-hydroxystyrene) and novolac. As both materials are polymeric phenols, the authors predicted *a priori* that these materials would absorb similar amounts of NMP in a given time. In fact, poly(*p*-hydroxystyrene) absorbs NMP at a rate 4 times that of novolac. Figure 8 shows that while these two polymers have similar solubility parameters, the 80 °C difference in T_g accounts for the difference in NMP uptake. The poly(*p*-hydroxystyrene) film has a T_g of 180 °C well above the 100 °C film baking temperature. However, T_g for the novolac film is the same as the 100 °C, bake temperature; hence, this film can undergo thermal annealing resulting in a reduced rate of NMP incorporation. The influence of annealing on poly(*p*-hydroxystyrene) films can be observed by measuring NMP uptake in a film baked at 100 °C as compared to a film baked at T_g (180 °C). In this side-by-side comparison, the film baked at 100 °C incorporated 950 ng of NMP while the film baked at 180 °C incorporated 589 ng (films stood for 15 min in an airstream containing 15 ppb NMP). This observation, that a film baked at T_g incorporated less NMP than a film baked 80 °C below T_g, is consistent with thermal annealing.

The plot in Figure 8 can also be used as an aid in designing new resist systems. From the features of the contour surface, we propose that NMP uptake will be minimized when a resist film is baked well above its T_g. One can further propose that NMP uptake will be minimized when the resist's matrix polymer is significantly more polar or less polar than NMP, and will be maximized when the polymer has a polarity near that of NMP. Let us consider the application of these guidelines to the design of new CA resist chemistry. Use of either a very polar or very non-polar polymer as matrix resin would be expected to reduce the degradation of resist performance caused by absorption of NMP vapor. However, a number of airborne substances already have been shown to degrade CA resist performance,[1-5] and it is likely that the complete set of such substances covers a wide polarity range. If so, then a shift in polymer polarity, while decreasing the absorption of one subset of contaminants, may well *increase* the absorption of another.

On that basis, we suspect that the optimization of resist thermal properties and processing conditions may prove a more general approach to minimizing contaminant effects. However, the impact of such optimization on other resist characteristics must be considered. For example, while the results in this paper suggest that simply postbaking above T_g will provide improved environmental stability, most CA resist chemistries in use today cannot be baked that high without degrading the imaging characteristics. In a similar fashion, the technologies used to transfer the relief image from the resist to the underlying substrate (such as plasma etching) demand that the final resist image have high thermal stability. This implies that the approach of using resist materials with lowered T_g is impractical. Therefore, the implementation of this means of stabilizing CA resists against degradation by environmental contaminants require the design of new resist materials based on polymers with high T_g's, but where the thermal stability of the formulation allows a postapply bake at temperatures at or above the T_g.

The thermal annealing aspect of this theory has been tested with isomers of poly((*tert*-butyloxycarbonyl)oxy)-styrene). The meta and para isomers of this polymer have glass transition temperatures of 90 and 135 °C, respectively. Both films were baked at 100 °C (above T_g for meta but below T_g for para) treated with 50–100 ppb NMP in air and subjected to a typical lithographic imaging process. The meta exhibited far greater image stability than the para isomer toward airborne contamination, consistent with thermal annealing of the meta film and thereby reducing the diffusion rate relative to that of the para film.[24]

Concluding Remarks

We have presented evidence that residual casting solvent is relatively unimportant in determining the propensity of a polymer film to absorb NMP. Films cast from different solvents but otherwise identical in composition and processing exhibit similar NMP absorption rates. Though residual solvent levels can vary widely depending on the characteristics of the polymer, rates of absorption of NMP vapor by the films are unrelated to the amount of retained solvent. We have provided evidence that polymer structural changes, rather than variations in

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residual solvent content, are responsible for the large changes in NMP uptake rates previously reported.

This study has provided information on the absolute quantities of NMP absorbed by polymer films from an airstream containing extremely low levels of NMP vapor. The method has allowed determinations of the absolute rates of NMP uptake under controlled conditions, and an absolute correlation of resist lithographic performance with NMP concentration of the film. Data have been presented which show how several process parameters influence the NMP content and uptake of such films. Interpretation of the NMP uptake data obtained for a series of different polymeric materials provides an understanding of how the polymer properties influence NMP absorption. With this understanding, it should prove possible to rationally select resins for chemically amplified resists so as to minimize the rate of absorption of NMP and other contaminants, thus reducing susceptibility to airborne contamination. Specifically the model presented in this paper suggests that contaminant absorption can be reduced in two ways: (1) absorption will be reduced if the CA resist system can be postapply baked at or above its T_g; (2) absorption will be reduced if a CA resist system can be designed with a solubility parameter significantly different from that of the airborne contaminant.

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