FUNDAMENTAL STUDIES OF AIRBORNE CHEMICAL CONTAMINATION OF CHEMICALLY AMPLIFIED RESISTS

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The susceptibility of most chemically amplified resists to performance degradation caused by low levels of airborne basic chemical substances presents a significant barrier to their practical implementation. We have carried out a series of systematic studies intended to improve our understanding of the mechanism of such degradation. We summarize here our investigation of how the contaminant/resist interaction is influenced by resist film composition. Our results suggest that contamination effects can be minimized by targeting specific ranges of physical properties when designing the matrix polymer.

1. Introduction

Resist systems based on acid-catalyzed chemical amplification (CA) have been used in the manufacture of microelectronic devices [1], and because of their unique properties it is likely such materials will find broader application in the future. A significant barrier to the widespread acceptance of CA resists is the difficulty of processing such materials in the presence of very low levels of airborne basic substances [2,3]. The lithographic effects of this airborne contamination have been well documented for several resists, but thus far the contaminant/resist interaction is understood at only a qualitative level. An improved understanding of the details of this interaction will assist the design of more robust CA resist systems, since if one can reduce contaminant absorption by the film, its effects on lithographic performance should be reduced proportionately.

In this paper we summarize the results of recent studies in our laboratory, which demonstrate how resist film composition can influence its susceptibility to airborne chemical contamination.

2. Experimental Methodology

The first reports of airborne contamination effects revealed that minute traces of volatile basic substances in the surrounding environment could produce profound (and disastrous) effects on the imaging properties of poly(4-t-BOC-styrene)-based resists [2,3]. Exceedingly low contam-

inant concentrations (in the 10 ppb range) are capable of causing observable lithographic effects. The study of contamination effects under controlled conditions representative of a manufacturing setting has been impeded both by the difficulties of producing a well-defined environment containing contaminant vapors at low concentration, and by the lack of a convenient means of quantifying contaminant absorbed in the resist film. We have constructed a test chamber that produces an airstream containing low but well-defined concentrations of contaminants, and have successfully applied radioactive tracer techniques in its use. This combination provides a quantitative method for the study of airborne chemical contamination.

The test chamber is a dynamic flow system first described by MacDonald and coworkers [2] (Figure 1). An activated carbon filter is attached to the inlet of a mechanical blower system, to produce two steady, high volume streams of chemically purified air. One airstream is then doped with the contaminant under study, by mixing with a low flow of nitrogen laden with contaminant vapor.

FIGURE 1. Dynamic flow system used in this study for the production of low concentrations of contaminant vapors.

The result is an airstream of known and reproducible composition suitable for quantitative experimentation. If required, the uncontaminated airstream can serve as a reference channel for

comparative studies. Each arm of the system produces an airflow of 30 ft³/min. By suitable adjustment of gas flow through the U-tube (see Figure 1), contaminant levels in the 5-100 ppb range can be readily attained.

In the studies we describe here, the airborne contaminating substance is 1-methyl-2-pyrrolidone labeled with the radioactive isotope ¹⁴C at the methyl carbon (abbreviated as NMP^{*}).

NMP^{*} was chosen for study because (1) it is widely used as a casting and stripping solvent in semiconductor manufacturing, (2) performance degradation of CA resists has been observed upon exposure to low concentrations of NMP vapor [4], and (3) it is readily available from a commercial source.

Radiochemical techniques offer unique advantages over alternative labeling schemes for trace analysis. Most importantly, the introduction of a radioisotope causes no change in the chemical properties of the analyte (except for a very small isotope effect which is insignificant in our experiments). An additional advantage is that the natural background level of radioactivity in air and in resist compositions is extremely low. Combined with the high sensitivity and efficiency of analytical methods for quantifying radioactivity, this facilitates detection of trace amounts of labeled analyte.

3. Kinetics of Contaminant Absorption

Figure 2(a) depicts the amount of radiolabeled NMP absorbed by a film of CA resist consisting of poly(4-t-BOC-styrene) and 5 % triphenylsulfonium hexafluoroantimonate photoacid generator, when stored for varying times in an atmosphere containing 10 ppb of NMP^{*} [5].

Also shown is the amount of NMP^{*} adsorbed on a bare silicon wafer when stored in the same airstream. The NMP^{*} content of the resist film increases with time in a nonlinear manner, while the amount of NMP^{*} adsorbed on silicon is low and essentially constant over the time of the experiment. After 30 minutes in the NMP airstream, the polymer film has absorbed ca. 750 ng NMP^{*}, or about 0.03 % of the total weight of the film.

FIGURE 2. (a) Absorbed NMP versus elapsed time for poly(4-t-BOC-styrene) + 5 % triphenylsulfonium hexafluoroantimonate resist. (b) NMP absorbed versus $(\text{time})^{1/2}$ for the resist.

For the case where a small molecule at low concentration diffuses through a glassy polymer, we expect to observe Fickian diffusion kinetics, wherein the total amount of NMP* absorbed increases with the square root of elapsed time [6]. Figure 2(b) plots the data in this manner, and shows a well-defined straight-line relation between absorbed NMP* and the square root of time. This suggests that NMP* absorption can be treated as a simple polymer/vapor permeation process, and that we can draw on the substantial body of work in the field of polymer permeability [7,8] in the interpretation of our experiments.

4. Compositional Effects on NMP Absorption

a. Effect of Photoacid Generator and Photoproducts

The effect of added photoacid generator (PAG) can be assessed by comparing the NMP uptake of polymer films formulated with and without added PAG but in all other respects prepared identically. We have tested resists based on two different polymer systems in this manner. With both systems we observe that the addition of PAG to a polymer film only weakly alters its NMP absorption properties. Figure 3 shows the amounts of NMP* absorbed by polymer films of differing composition after storing for 15 minutes in a 10 ppb NMP* airstream.

In all cases, the added PAG reduces NMP uptake by ca 15 %. Similar reduction is seen for both ionic and nonionic PAGs. This may be attributable to a change in the overall polarity of the

Polymer	Acid Generator	NMP Content (ng/wafer)	
		Unexposed	Exposed
$\text{-(CH}_2\text{-CH)}_x\text{-}$	none	578	—
	$\text{Ph}_3\text{S SbF}_6$	487	703
	none	689	—
$\text{-(CH}_2\text{-CH)}_x\text{-(CH}_2\text{-CH)}_y\text{-}$	$\text{Ph}_3\text{S SbF}_6$	583	729
	570	689

FIGURE 3. Effect of photoacid generator and photoproducts on the NMP absorption properties of resist films.

matrix caused by the added PAG (see later discussion below). Figure 3 also lists NMP uptake data for identical polymer/PAG films which were exposed with deep-UV light at a dose of 10 mJ/cm² before placement in the NMP airstream. This dosage approximates that required for imaging these formulations. In all cases, a slight increase in rates of NMP absorption is detected. This may be a consequence of the change in overall polarity induced by the photo-reaction, the acid-base interaction of the photoacid with the absorbed NMP*, or may result from other physical changes in the matrix which facilitate diffusion of the permeant into the polymer film [9].

b. Effect of Residual Solvent

The rate of NMP uptake by polymer films is determined in part by the ease with which the contaminant diffuses through the film. It is well known that the mobility of small molecules in polymeric materials can be strongly affected by the concentration of solvent in the matrix [8]. Other laboratories have reported effects of residual casting solvent on diffusion in CA resist films. One study showed that significantly different image profiles were obtained depending on the casting solvent [10]. More direct evidence of residual solvent effects on diffusion has been reported by workers from Hitachi [11]. Their work demonstrated that the diffusion range of acid in resist films changes sharply with the level of retained casting solvent. In like manner, one anticipates that differing levels of residual casting solvent might lead to similar differences in NMP absorption rates.

We tested for such an effect by first precisely measuring levels of residual solvent in a set of polymer films of widely varying structural characteristics, and then correlating NMP absorption rates of those materials with their solvent contents [12]. Solvent residue was quantified by preparing spin-cast films from solutions containing radiolabeled propylene glycol monomethyl ether acetate (PGMEA) casting solvent, and determining the level of residual radioactivity in each film following a post-apply bake under standard conditions (100 °C/5 min). NMP uptake was determined using the radiotracer method described earlier. Chemical structures of the polymers studied, their residual solvent contents, and their NMP absorption rates are summarized in Figure 4.

No relation between solvent level and NMP absorption is apparent. While the amount of casting solvent residue clearly increases with increasing polymer polarity, the NMP uptake behavior does not follow a similar trend. Closer inspection of these NMP uptake data *does* disclose the importance of *structural* effects, however. Small variations in polymer chemical structure can lead to surprisingly large changes in rates of NMP absorption. Compare, for example, the NMP uptakes of novolac and poly(hydroxystyrene) films, which differ by a factor of six, or the NMP uptakes of poly(4-t-BOC-styrene) and poly(3-t-BOC-styrene) films, which differ by a factor of seven. Within each pair, the polymers are constituted of identical functional groups and are simply positional isomers. We more closely examine below the cause of this variation in NMP absorption.

c. Effect of Polymer Structure

The NMP vapor absorption properties of a set of twenty-four different polymeric materials were studied under identical conditions [13]. This materials set was chosen so as to incorporate the

POLYMER	STRUCTURE	RESIDUAL SOLVENT (WT %)	NMP CONTENT (ng/water)
Epoxy Novolac		0.05	10
P(meta-TBOCST)		0.5	120
P(para-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(para-HOST)		20.4	1605
Cresol Novolac		21.1	268

FIGURE 4. Comparison of residual solvent contents and NMP absorption properties for a series of polymers. All films were spin-cast and post-apply-baked at 100 °C for 5 min to give final film thicknesses of 1 μ m.

widest practical range of functionality. The polymers, physical properties, and their NMP contents following storage for 15 minutes in a 12 ppb NMP^{*} airstream are listed in Figure 5.

A wide variation of absorption behavior is evident, ranging from essentially no NMP absorption (e.g. for epoxy-novolac and some methacrylate esters), to comparatively high rates of NMP absorption (e.g. for certain poly(hydroxystyrenes)).

The vapor and gas permeability of polymer films is generally treated in terms of the solution diffusion model [7], in which the vapor is first sorbed onto the surface of the film in a rapid equilibration and then slowly diffuses into the bulk polymer. In this model, permeability is controlled both by the solubility of the permeant in the film, and by the diffusivity of the

Polymer	NMP Content (ng/wafer)	Solubility Param. (cal/cm ³) ^{1/2}	T _g (°C)
poly(methylmethacrylate)	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
poly(styrene)	64	8.5	100
epoxy cresol 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(t-Bu-vinylbenzoate)	882	9.6	160
poly(3,5-Me ₂ -4-t-BOC-styrene)	362	9.9	130
poly(t-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-t-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

FIGURE 5. Listing of polymers examined in the study of polymer structural effects on NMP absorption. Also listed are polymer T_g, solubility parameter, and NMP content after storage in a 12 ppb NMP* airstream for 15 minutes.

permeant through the film. The solution diffusion model provides a useful framework for analyzing our experimental data.

I. POLYMER/PERMEANT SOLUBILITY. The equilibrium solubility of NMP in each of these films is readily characterized by comparing its reported solubility parameter with those determined for each polymer. A correlation of our NMP uptake measurements with polymer solubility parameters is shown in Figure 6(a).

FIGURE 6. (a) Amount of NMP* under equivalent conditions by various polymers as a function of the solubility parameter of the polymer. The solid line represents a fourth order polynomial fit to the data. (b) Amount of NMP* absorbed under equivalent conditions by various polymers, as a function of the glass transition temperature of the polymer. The solid line represents a second-order polynomial fit to the data.

While there is much scatter, the data shows a maximum in NMP* uptake for polymers with solubility parameters near that of NMP, and low rates of NMP* uptake when the polymer is very polar or very non-polar compared to NMP. While the plot provides evidence that solubility is one factor influencing NMP* absorption, the scatter suggests other factors are also important.

FREE VOLUME EFFECTS. The presence of free volume in a polymer matrix is considered to strongly influence the diffusivity of small molecules within it [7]. During spin-coating, large amounts of free volume are created in thin polymer films such as photoresists [14]. The amount of free volume can be reduced by annealing the film after spin-coating at a temperature near or above the glass transition of the polymer. Our materials set contains polymers having T_g values that range from slightly above room temperature to greater than 200 °C. Since all films were post-apply baked using identical conditions (100 °C, 5 min), the tested films were baked above, below or at their T_g depending on properties. Figure 6(b) shows the correlation

of NMP uptake with polymer T_g . Again some deviation is seen, but the general behavior supports the idea that T_g (and therefore excess free volume) is a second important factor influencing NMP absorption.

FIGURE 7. Amount of NMP* under equivalent conditions by various polymers as a function of both the solubility parameter of the polymer and the glass transition temperature of the polymer. The surface shown is polynomial least-squares fit to the data.

Figure 7 shows a three dimensional surface plot of both solubility parameter and T_g versus NMP absorption. When represented in this manner, all data at hand are accounted for, with no anomalous outlying points. This indicates that both polymer/permeant solubility and free volume are equally important determinants of the NMP uptake characteristics of thin polymer films. While many other factors can influence polymer permeability [7], the absence of outlying points suggests that, by considering only solubility and free volume, NMP absorption behavior can be predicted with a reasonable level of accuracy. Thus the relationship shown in Figure 7 should prove useful for predicting the behavior of as-yet-unttested polymers.

5. Summary

We have applied radiochemical labeling techniques to the detection of trace levels of airborne contaminants absorbed by polymer films. Using a dynamic flow system to achieve low vapor concentrations, we have carried out a controlled study of the relation between contaminant absorption and the composition of chemically amplified resists. We find in this study that

polymer properties, in particular the solubility of the contaminant in the polymer, and the T_g of the polymer relative to the post-apply bake temperature, strongly influence the contaminant uptake of a resist film. By controlling these properties through appropriate materials design, it should prove possible to develop new CA resists with improved resistance to environmental contaminants.

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