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Thermal Analysis of Positive Photoresist Films by Mass Spectrometry

Abstract: Mass spectrometry is used to monitor the effect of temperature on positive photoresist and its two major components, a base resin and a photoactive compound. This technique is also used to identify the photolytic products of photoresist by exposing it in situ to ultraviolet radiation and to identify the resulting volatile products when it is heated after exposure. Quantitative data are obtained for the two major thermal products of photoresist, and the activation energy is calculated for the thermal degradation of the photoactive compound.

Introduction

In the coating of solid films of positive photoresist, the prebake temperature is an important processing parameter in controlling not only the thickness and uniformity of the resist film but also its response to ultraviolet radiation exposure. Dill and Shaw [1] demonstrated that a decrease in film thickness occurred as a function of increasing bake temperature. A constant thickness plateau was reached, for each of three temperatures, that was independent of further bake time. They also demonstrated that prebake processing can destroy the optical sensitivity of the resist. A prebake of 100°C for one hour, as compared to a 70°C prebake, destroys 50 percent of the optical sensitivity of the resist, and a 130°C prebake destroys 97 percent of this sensitivity. The decrease in thickness at increasing prebake temperatures was hypothesized as being due not only to residual solvent loss but also to volatile products released during the thermal degradation of the photoresist.

A post-exposure bake process [2], i.e., a bake step inserted before development of the exposed image, recently has been used to reduce the standing wave fringes that occur in developed resist patterns when monochromatic light is used in the exposure. When a low prebake of 70°C is accompanied by a high post-exposure bake of 100°C, a diffusion of exposure products results in an almost total reduction of these fringes. A bake after exposure also results in the visualization of the exposed image, which prior to this process had not been discernible to the eye.

No information is currently available on what vapor species are released during the prebake or post-exposure bake treatments and on the temperature range in which they are significant. Further, no kinetic data exist on the reactions involved that would permit optimization in the processing of photoresist films. We therefore decided to examine in detail the thermal and kinetic properties of the photoresist system by applying a mass spectroscopic technique developed at this laboratory by M. A. Frisch [3]. In addition to these studies, we also hoped to gain insight into the possibility of using this mass spectroscopic technique for a quantum yield measurement, by exposing the photoresist to ultraviolet light in the mass spectrometer and monitoring the volatile exposure products.

Experimental techniques

The photoresist investigated is Shipley AZ1350J [4] (Lot No. A30036J), a positive resist composed of approximately 20 ± 2 weight percent photoactive compound (a diazo oxide), to which we refer as PAC, and the remainder a photolytically stable resin (a cresylic acid-formaldehyde Novolak polymer). These resist constituents are dissolved in a solvent system consisting of 70 percent Cellosolve acetate (2-ethoxy-ethyl acetate, b.p. 156°C), 11 percent n-butyl acetate (b.p. 126°C) and 19 percent xylenes (b.p. 138° to 144°C). This photoresist was further diluted 2:1 with this same solvent system, Shipley AZ thinner [4], and spin coated on silicon substrates 0.9 cm diameter. Thickness measurements were made before and after mass spectral analysis utilizing IOTA, a computerized spectrophotometer [5]. Before in-situ thermal analysis and exposure to ultraviolet radiation, the samples were degassed overnight at 3×10^{-9} Torr (4×10^{-7} Pa).

Table 1 Major mass peaks and their relative intensities. Data are cited relative to the largest peak, $m/e = 43$.

Major peak, m/e	*Type of sample: relative intensity* Cellosolve acetate[a]	Cellosolve acetate[b]	*Group I coated wafer (no prebake)*	*Group II coated wafer (prebake)*
29	24	24	10	10
31	34	39	30	26
43	100	100	100	100
44	25	25	28	23
45	12	10	12	12
59	30	31	44	39
72	28	21	20	19

[a] *Index of Mass Spectral Data* [8].
[b] *Registry of Mass Spectral Data* [9].

The mass analysis is performed on a computer controlled, high-temperature mass spectrometer system (HTMS) [6], equipped with a Knudsen effusion cell. When a solid sample is heated in this cell a molecular beam is produced which effuses through the cell orifice. For this application a special molybdenum Knudsen cell was fabricated. A nickel-chrome heater, encapsulated in an electrically insulated jacket, was wound tightly around the cell circumference. This construction provided the required close coupling of the power source to the cell walls for precise temperature control. The inside bottom surface was ground flat to insure good thermal contact of the photoresist coated silicon wafers with the cell. The Pt + 10 percent Rh vs Pt thermocouple, used for both temperature measurement and control, is secured in the center of the cell bottom within one mm of the sample. The thermocouple voltage is read on a Leeds and Northrup precision digital voltmeter providing 100 nV resolution. The cell orifice, approximately one mm diameter and five mm in length, has a conductance of 27 cc/s for nitrogen at 400 K. The volume of the cell is 1.3 cc, which gives a characteristic pumping time of 0.05 s. This residence time is sufficiently small to provide faithful representation of the reaction process even at high reaction rates, permitting use of the ion signals directly without differentiation. The molecular beam effusing through the cell orifice is modulated at 20 cps before entering the ion source of a quadrupole mass spectrometer. The mass spectra are obtained using a low ionizing energy of 30 volts to minimize the contribution of the more highly fragmented ions to the spectra, while maintaining nearly full signal sensitivity for the major ion peaks. The spectrometer is in a differentially pumped ultrahigh vacuum chamber ($<10^{-10}$ Torr) having minimum background interference. The coherent ion signal, arising from the vapor species in the Knudsen cell, is derived from computer demodulation of the ion pulses, obtained from two separate 100-MHz scalers, gated to count in and out of phase, respectively, with the interruption of the beam. An IBM 1800 computer controls all essential operating parameters of the system; namely, mass range, mass position, electron energy, and ion energy of the mass spectrometer; integration time, scalar readout of the ion counting subsystem, and digital voltmeter set point and readout of the temperature measurement and control subsystem.

The mass spectrometric technique has several limitations. It is a destructive method which thermally decomposes the sample to be analyzed. This sample must be stable at room temperature and present in sufficient amount to give large enough ion signals for identification. In the HTMS mass spectrometric system used in this analysis, 10 to 100 nanograms of the specimen material was sufficient, depending on the cracking pattern of the molecule. Also the temperature controller used in heating the sample must be stable and reproducible. The HTMS is capable of scanning a temperature range from room temperature to 800°C at a minimum rate of 0.1°C/min up to a maximum rate of 16°C/min.

The ultraviolet source used to expose the photoresist was a Hanovia high-pressure mercury arc in which the strongest line occurs at 365 nm. The molybdenum cover of the Knudsen cell was replaced with a quartz disk to permit direct illumination of the photoresist sample through the vacuum viewport. The total absorption through these windows was less than 10 percent in the region 330-3000 nm. The total absolute light intensity (330-1300 nm), measured in the plane of the silicon substrate with a radiant fluxmeter, was 0.25 mW/cm^2. Throughout the course of these experiments, care was taken to protect all samples from extraneous ultraviolet and infrared irradiation by placing suitable filters over the viewports on the vacuum system.

The photoresist coated wafers were divided into three groups. Group I includes all samples that were not prebaked. These retain residual solvent, although a certain amount of solvent loss (approximately three percent of the film weight) occurs in the overnight degassing process in the HTMS. The wafers were gradually heated from 25°C to 170°C at a rate of 1°C/min while the unit masses 12-250 were repetitively scanned every 112 s. Group II wafers were first prebaked in a circulating air oven at 70°C for 1/2 hour and then analyzed as above. The Group III wafers include two prebaked samples that were exposed to ultraviolet radiation while the resulting volatile products were simultaneously monitored. The first of these samples was exposed to ultraviolet for 40 min and subsequently heated in the mass spectrometer at a preprogrammed rate, as described above. The second wafer was exposed only to radiation and four

Table 2 Percent thickness loss of photoresist after prebake and after thermal mass analysis.

	Type of sample				
	Group I (no prebake)		*Group II (prebake)*		
Initial thickness (Å)	7201	16935	6973	7204	7744
Loss after prebake, percent	N.A.	N.A.	9.8	7.2	10.5
Loss after thermal analysis, percent	20.0	23.2	11.2	12.8	11.1
Total loss, percent	20.0	23.2	21.0	20.0	23.1
Weight loss ratio, thermally produced N_2 to Cellosolve acetate	1:10.7	1:11.6	1:6.8	1:6.5	1:7.0

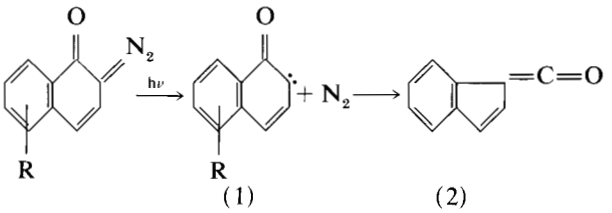
ions (mass peak 12, 14, 18, 28) were scanned every 40 s to examine in more detail the photolytic decomposition of the photoactive compound.

In addition to our study of these wafers, we also analyzed the two solid components of the photoresist mixture. The first was a purified sample of the photoactive compound (1-oxo-2 diazo-naphthalene-5-sulfonic acid ester of trihydroxyarylphenone) and the second was a sample of the resin (cresylic acid-formaldehyde Novolak polymer) [7]. This resin was purified by heating in a vacuum at a temperature higher than that employed in this study. Each sample (approx. one mg) was weighed in a tungsten cup, analyzed in the same Knudsen cell under conditions identical to those employed with the photoresist films, and later reweighed to obtain weight loss data for absolute calibration of the integrated ion signals. The cover of the Knudsen cell was also weighed to determine that no material had condensed on the cooler surface. The precision in these weight measurements was better than five μg. The typical results reported below were data acquired from multiple reproducible sample analyses.

Results

• *Mass analysis of thermal products of photoresist films*
Of the masses scanned, only those ions associated with Cellosolve acetate and nitrogen were observed in significant quantities. Thus Cellosolve acetate is the only residual solvent in the photoresist films. No trace levels could be detected for the other solvent constituents, n-butyl acetate or xylene, and we assume that these more volatile components of the solvent system were removed either in the initial prebake or during the overnight degas procedure. Our identification of Cellosolve acetate as the major product was confirmed by comparison with data in *The Index of Mass Spectral Data* [8] and a computerized search of the *Registry of Mass Spectral Data* [9]. Table 1 compares the published spectra of Cellosolve acetate with Group I (no prebake) and Group II (prebake) photoresist samples. The major mass peaks are tabulated relative to the largest peak (base) appearing in the spectrum ($m/e = 43$). The major discrepancies are reflected in the more highly fragmented species (e.g., $m/e = 29$) because of the difference in ionizing energy used in the HTMS at 30 v and that reported in the literature at 70 v. Table 2 summarizes the percent thickness loss after both the prebake and thermal mass analysis, and the resulting ratio by weight loss between the thermally produced nitrogen and the Cellosolve acetate.

The source of the signal at $m/e = 28$ is believed to be due only to nitrogen gas arising from the thermal decomposition of the PAC. No significant CO contribution could be detected, as evidenced by the absence of the C_{12}^+ fragment. The purified PAC, described in a later section, was 100 times larger than the concentration in the photoresist films, and the mass spectra displayed no in-phase signal at $m/e = 12$. This observation lends support to our interpretation that no CO is generated because of the thermal decomposition of PAC in the resist film. However, we did observe a measurable signal for the N_{14}^+ species in the correct abundance ratio of approximately one percent, which confirms our nitrogen assignment. The detection of nitrogen as the only gaseous decomposition product of PAC suggests a thermal mechanism identical to the photolytic mechanism suggested by Sus et al. [10] in the following reaction:



(1) (2)

Because no other volatile species, specifically CO and CO_2, were detected, we assume the unstable carbene(1) or ketene(2), postulated in the above reaction, must form new products that are thermally stable up to

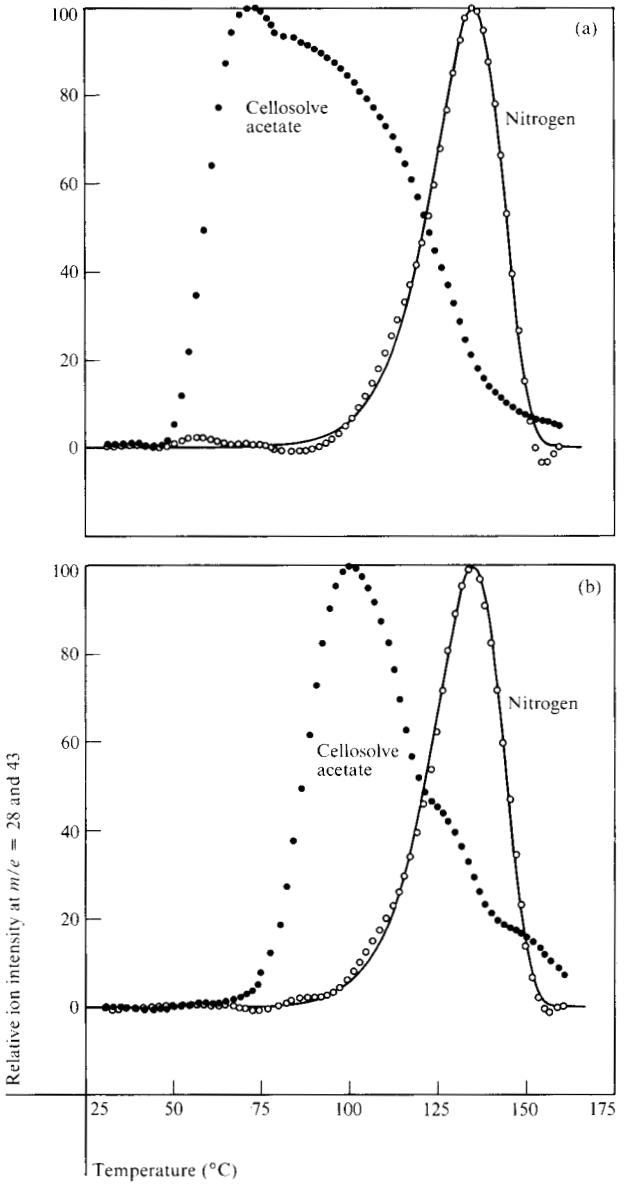


Figure 1 Evolution of Cellosolve acetate and nitrogen vs temperature, in °C. (a) Without prebake. (b) With prebake.

170°C, the maximum temperature of our measurements. A paper by Yates and Robb [11], in which they studied the thermal decomposition of diazo oxides in solution, supports this conclusion. When a naphthalene-2,1-diazo-oxide was refluxed in a xylene solution, a dimer was isolated in high yield which represented the reaction between a thermally produced carbene and ketene.

Figure 1(a) (no prebake) and 1(b) (prebake) are plots of the base peak of Cellosolve acetate ($m/e = 43$) and the parent ion of nitrogen ($m/e = 28$) vs temperature °C. To better illustrate the evolution of Cellosolve acetate and nitrogen as a function of sample temperature, all peaks have been normalized to 100. However, the Cellosolve acetate signal is 10 times greater than nitrogen for the no-prebake sample, and six times greater for the prebake sample. The signal at $m/e = 28$ was corrected for a small contribution (1.4 percent) of the $m/e = 43$ intensity from the fragmentation of the Cellosolve acetate. As can be seen for the no-prebake sample, the Cellosolve acetate evolves continously between 50° and 160°C, reaching a maximum rate at 65°C. In the case of the prebaked wafer, the evolution of Cellosolve acetate occurred between 70° and 160°C, reaching a maximum rate at 98°C. The shape of these peaks, in particular for the prebaked film, indicates that there exist at least three overlapping binding energy states, each of these having a different activation energy. At high concentrations of Cellosolve acetate, where excess solvent molecules are loosely bonded to the PAC or resin, only low temperatures are required to remove these molecules. However, as the solvent concentration decreases, increasingly higher temperatures are required to remove the molecules strongly bonded to the resist system. The shift in the peak desorption rate for Cellosolve acetate between the non-baked and prebaked films is evidence that the lower energy states are not repopulated upon standing.

Significant evolution of nitrogen, due to the decomposition of the photoactive compound, was observed between 98° and 160°C, the rate peaking at 135°C, for both the no-prebake and prebake samples. The nitrogen signal decayed rapidly after evolution reached a maximum rate at 135°C, indicating a first-order reaction. In a first-order reaction 63 percent of the ions is evolved by the maximum rate, as opposed to 50 percent for a second-order reaction. The activation energies and reaction orders for these decomposition reactions were calculated by the method described by M. A. Frisch [3]. They are derived from the best fit of the ion current vs temperature data to an integrated rate equation. In Figs. 1(a) and 1(b), the experimental data for nitrogen are represented by squares and the theoretical curve by the solid line. The non-prebaked and prebaked films gave the same activation energy (33 Kcal/mole), and the same temperature of maximum reaction rate (135°C). Thus no measurable change in the PAC stability is observed when these photoresist films are prebaked at 70°C.

• *Mass analysis of photoresist components*

The photoactive compound PAC was also analyzed under the same conditions as the films, but we scanned over a wider mass range (12-465) in order to insure that no high molecular weight species were volatilized in our temperature range. The sample lost 10.4 percent by weight after thermal analysis. The majority of this

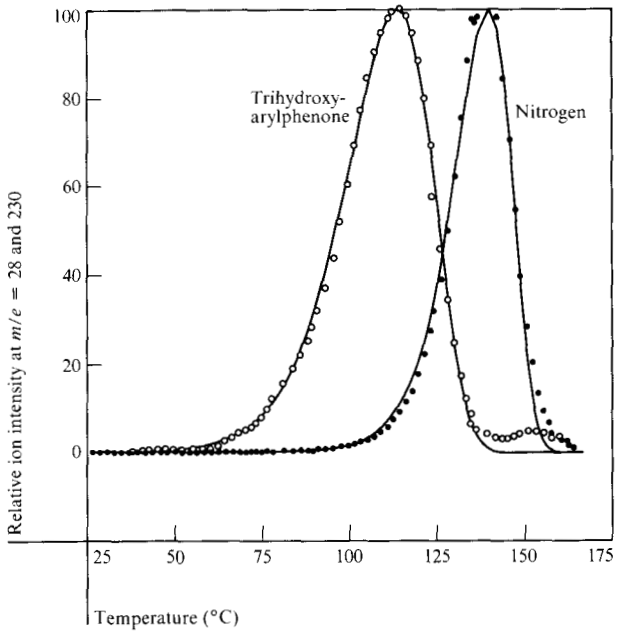
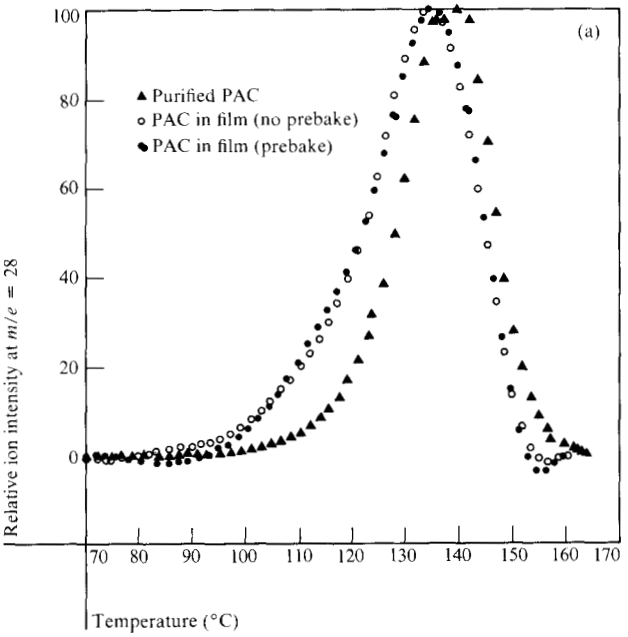


Figure 2 Major thermal decomposition products of purified PAC photoactive compound.



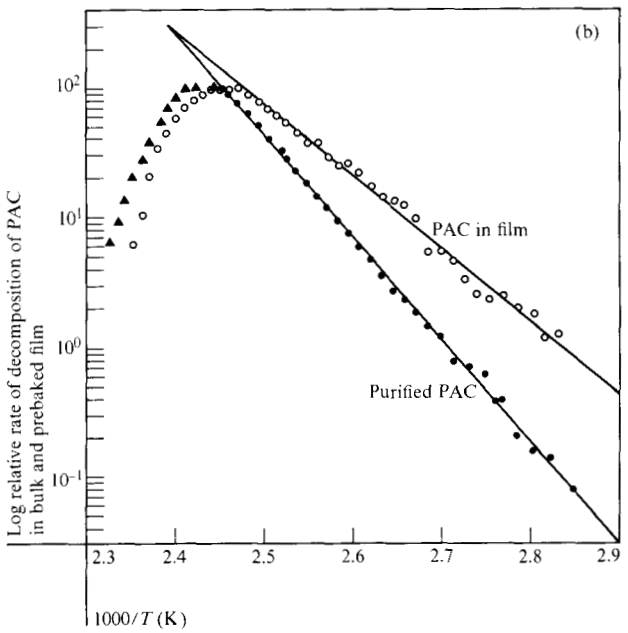


Figure 3 (a) Linear plot comparing the nitrogen signal from purified PAC and the photoresist films, prebaked and non-prebaked. (b) Logarithmic plot of the nitrogen signal, comparing the relative rate of decomposition for the PAC in the photoresist film and in the purified material vs 1000/T, in K.

weight loss (8.4 percent) was due to nitrogen and 1.5 percent to trihydroxyarylphenone (M.W. = 230), whose cracking pattern is similar to those of isomers reported in *Registry of Mass Spectral Data* [9]. The remaining 0.5 percent was due to an unidentified peak at $m/e = 58$ and a peak at $m/e = 48$, which we associate with the SO^+ ion. The weight percentage of nitrogen and trihydroxylaryphenone in the PAC essentially accounts for the weight-loss data. Thus the sum of all the other volatile products released up to 170°C are at least a factor of ten smaller, by weight, than the nitrogen contribution. This evidence further substantiates the mass spectral data that the reaction products formed upon the release of nitrogen are not volatile in the temperature range of our study.

Figure 2 is a plot of the ion signals for nitrogen and the parent ion of trihydroxyarylphenone ($m/e = 230$) vs temperature. The shape of both these curves is indicative of a first-order reaction and they do not show the multiple structure observed for Cellosolve acetate desorption. As in the previous figures, the theoretical curve overlays the experimental points, and the data is normalized to 100. The activation energy for the decomposition of PAC, releasing nitrogen gas, is 40 Kcal/mole, with the maximum reaction rate occurring at 139°C. For the desorption of trihydroxyarylphenone, an impurity in the PAC sample, the calculated activation energy is 23.5 Kcal/mole with a maximum desorption rate at 114°C. Thus we find that the PAC in the photoresist film is less stable (33 Kcal/mole) than the purified PAC (40 Kcal/mole). Figure 3(a) is a linear plot of the nitrogen signal from the purified PAC and the photoresist film (prebaked and non-prebaked), showing the tendency of the PAC in the film to decompose at lower temperatures. In Fig. 3(b), we have plotted the logarithm of the relative decomposition rate of PAC for

Table 3 Summary of thermal analysis of photoresist and its components.

Major peak	*Assoc. species*	*Type of sample*					
		Prebake wafer		*PAC (Diazo oxide)*		*Base resin (Novolak)*	
		T_{max}, °C	*Weight percent*	T_{max}, °C	*Weight percent*	T_{max}, °C	*Weight percent*
10	H_2O	–	–	–	–	120°	1.5
28	N_2	135°	1.6	135°	8.4	–	–
	Cellosolve acetate	98°	10.2	–	–	–	–
48	SO	–	–	140°	0.2	–	–
58	?	–	–	125°	0.3	–	–
107	Monomer	–	–	–	–	145°	1.0
228	Dimer	–	–	–	–	166°	0.8
230	Trihydroxy-arylphenone	–	–	113°	1.5	–	–
	Total weight loss, percent	–	12.8	–	10.4	–	3.3

both the pure material and prebaked film. In the case of the pure PAC, there is a change of three orders of magnitude in the rate over the region 75° to 139°C.

The base resin (cresylic acid-formaldehyde Novolak polymer) lost three percent by weight after HTMS analysis under conditions identical to those applied to the films. The major volatile product present was H_2O, which evolves between 75° and 120°C. The remaining mass fragments were released above 125°C and are indicative of the cracking pattern for the polymer. At 145°C the largest of these remaining mass fragments is $m/e = 107$, which is the monomer unit of the polymer ($C_7H_7O^+$). We also see a mass fragment at 228 m/e ($C_{15}H_{16}O_2^+$) which we associate with the dimer. No volatile ions were observed at lower temperatures due to the effective purification of the resin by heating at high temperatures under vacuum.

Table 3 is a summary of the thermal analyses of the photoresist and its components. The weight loss of the major products, Cellosolve acetate and nitrogen, have been quantitatively determined by calibration of the photoactive compound and thickness loss measurements. The minor products have been estimated from the peak relative ion intensities. For the prebaked wafer, one percent of the weight loss remains unidentified.

- *Mass analysis of the exposure products of photoresist films*

A prebaked photoresist sample was exposed to ultraviolet radiation at room temperature in the mass spectrometer. Only nitrogen and its associated fragment ion were observed. For the sample shown in Fig. 4 only the masses 12, 14, 18 and 28 were monitored to follow the photolytic reaction with a better signal-to-noise ratio. The fragment ions 12 and 14 were specifically measured to prove that the source of the signal at $m/e = 28$ was due only to nitrogen. No measurable contribution could be attributed to CO. The nitrogen production decays and ceases entirely when the ultraviolet source is removed. This wafer showed no thickness loss after the exposure. A second prebaked wafer was exposed and subsequently heated in situ and the entire mass range was scanned (12-250). Nitrogen appeared at room temperature because of exposure, and subsequent heating released Cellosolve acetate and additional nitrogen because of the partial irradiation of the diazo compound. No new mass fragments were observed and the spectrum is very similar to that in Fig. 1(b). We assume that all of the nitrogen caused by exposure has diffused through the film, as we see no signal at $m/e = 28$ other than that thermally produced by the fragmentation of the PAC.

Figure 5 compares the evolution rate of Cellosolve acetate vs temperature (°C) for Group I, II and III photoresist samples. Both the non-prebaked and the prebaked resist display similar slopes although, as can be expected, the evolution of Cellosolve acetate occurs at a lower temperature for the non-prebaked sample. However, for the prebaked sample which was exposed and then heated, the evolution of Cellosolve acetate appears at lower temperatures and with a different slope than that of the unexposed prebaked sample. This strongly suggests that exposure to radiation releases Cellosolve acetate from the higher energy bonding sites in the photoresist and repopulates those at lower energies, which are normally removed by the prebake treatment.

This finding may be one reason why an exposed image becomes visible after a post-exposure bake. The solvent remaining in the exposed area is removed at a different rate than in the unexposed resist, resulting in a thickness change that is discernible to the eye. After a post-exposure bake treatment, the image resulting from a heavy exposure in the central area of a photoresist coated sili-

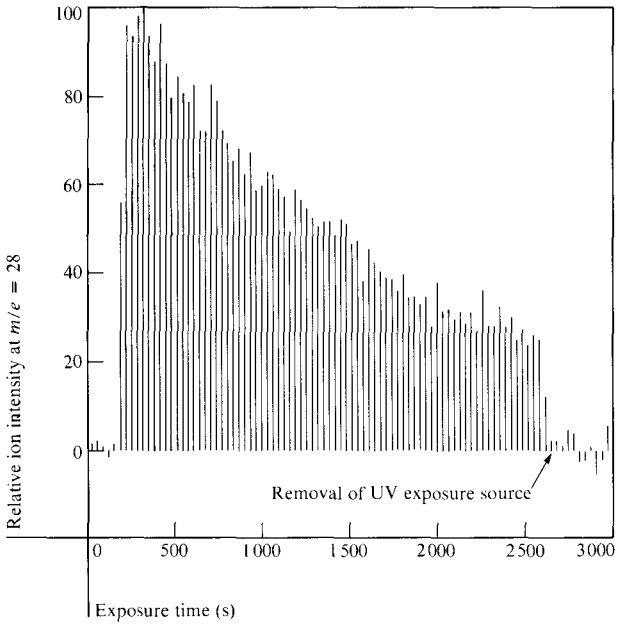


Figure 4 Evolution of nitrogen from a photoresist film upon exposure to ultraviolet radiation.

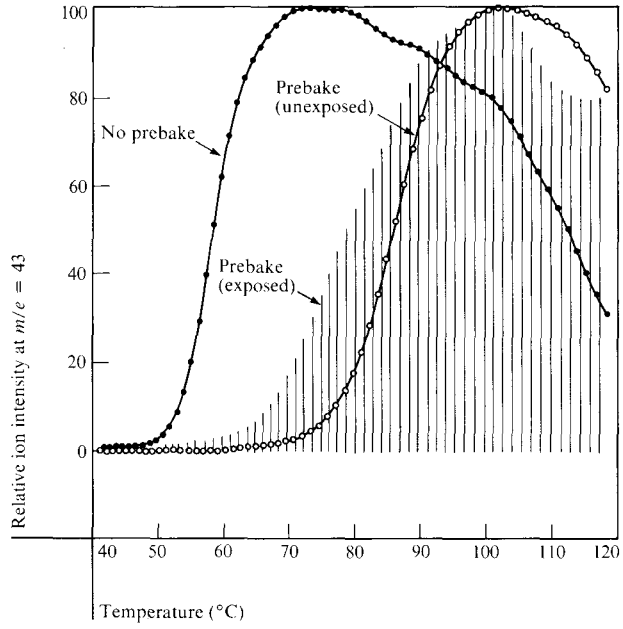


Figure 5 Comparison of the desorption of Cellosolve acetate in unexposed photoresist films with that in exposed films.

con wafer was two percent thinner than the surrounding unexposed resist. As there was little thickness loss when the sample was measured after exposure (0.3 percent), we attribute the majority of the thickness loss after post-exposure bake to the different activation energies between the solvent in the exposed and unexposed photoresist.

Conclusions

The residual solvent in the resist has been identified as Cellosolve acetate. This solvent is so strongly bonded to the resist system that it requires temperatures near its own boiling point for complete removal. Normal prebake processing will not eliminate Cellosolve acetate, and higher prebake temperatures will destroy the photoactive compound. The loss of the thickness seen in normal prebake processing (70-100°C) is due mainly to the Cellosolve acetate, with very minor contributions from the degradation of the polymer and the photoactive compound. The thermal release of nitrogen is a first-order reaction for both photoresist films and the pure photoactive component. A significant rate of decomposition of the photoactive compound occurs at 100°C, the maximum rate of decomposition occurring at 139°C. The PAC in the resist film is less stable than a sample of the purified material.

The major effect of a low prebake at 70°C and a high post-exposure bake at 100°C is to eliminate residual Cellosolve acetate. The Cellosolve acetate desorbs at a lower temperature and at a slower rate for the exposed resist than the unexposed, and it seems likely that this solvent acts as a carrier of exposure products from regions of high density to those of lower density, thus eliminating standing waves in monochromatically exposed photoresist.

In order to obtain a quantum yield measurement of the photoresist, further experiments must be performed utilizing a more intense exposure source so that the reaction will go to completion. This measurement is feasible, however, because of the complete diffusion of nitrogen through the resist.

We have found this mass spectrometric method to be a powerful tool in quantifying the kinetic and thermal properties of photoresist films and its components, and in monitoring its exposure products. It might also be used to monitor the chemisorption of photoresist adhesion promoters on silicon substrates.

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References and notes

1. F. H. Dill and J. M. Shaw, "Thermal Effects on the Photoresist AZ1350J," *IBM J. Res. Develop.* **21,** 210 (1977, this issue).
2. E. J. Walker, "Reduction of Photoresist Standing Wave Effects by Post-Exposure Bake," *IEEE Trans. Electron Devices* **ED-22,** 464 (1975).
3. M. A. Frisch, "Kinetic Study of Heterogeneous Reactions by Linear Temperature Programming," *24th Conference on Mass Spectrometry and Allied Topics*, San Diego, California, May 9-14, 1976.
4. Registered trademark of the Shipley Company, Inc., Newton, MA 02162.
5. K. L. Konnerth and F. H. Dill, "IOTA, A New Computer Controlled Thin Film Thickness Measurement Tool," *Solid-State Electron.* **15,** 371 (1972).
6. M. A. Frisch, paper presented at *23rd Conference on Mass Spectrometry and Allied Topics*, May 20-25, 1973.
7. These materials were supplied by P. Hood, IBM System Products Division laboratory, East Fishkill, New York.
8. *Index of Mass Spectral Data*, 1st ed., American Society for Testing Materials, Philadelphia, PA, July 1963.
9. E. Stenhagen, S. Abrahmsson (University of Gothenburg), and F. W. McLafferty (Cornell University), Eds., *Registry of Mass Spectral Data*, 4 vols., John Wiley and Sons, Inc., New York, 1974.
10. O. Sus, J. Munder, and S. Kalle, *Angew. Chem.* **74,** 985 (1962).
11. P. Yates and E. W. Robb, "The Thermal Decomposition of the Diazo Oxides," *J. Amer. Chem. Soc.* **79,** 5760 (1957).

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