Solubility of Carbon Dioxide and Cosolvents in a Photoresist Polymer

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ABSTRACT: Solubility and diffusivity of cosolvents and carbon dioxide in a photoresist polymer have been measured below the glass transition temperature by the inverse gas chromatography and static capsule methods over a temperature range of 75–100°C and pressures up to 7000 kPa. The results showed that presence of even low pressures of CO_2 increased the solubility and diffusivity of the cosolvents studied. Experiments in which exposure of the polymer to CO_2 was cycled on and off indicated that the free volume introduced by the CO_2 persisted in the polymer for a significant time after removal of the CO_2. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1865–1870, 2008

Key words: diffusion; photoresists; swelling

INTRODUCTION

The primary objective of this research was to evaluate the potential of a carbon dioxide–cosolvent system for the removal of polymer coatings in electronic chip manufacturing. Carbon dioxide is the most commonly used supercritical fluid because of its low cost and environmental impact. Its small size allows it to penetrate into a polymer more easily than larger liquid solvents. The swelling of the polymer and the diffusion of the CO_2 and cosolvents are important parameters in the removal process.

This publication presents experimental results for the solubility and diffusivity of CO_2 and a number of cosolvents in a photoresist polymer that was essentially a polymethacrylate backbone with reactive (2-alkyl-2-adamantyl) and etch-resistant (3-hydroxy-1-adamantyl) pendant groups attached. The polymer was obtained from the Sumitomo Chemical Company, Tokyo, Japan, and had a molecular weight of 11,000 g/mol, a dispersion index of 1.8, and a density of 1.22 g/cm^3. These are typical values for this generation of 193 nm resist. The T_g of the polymer was approximately 150°C.

The study involved a two-prong experimental approach using inverse gas chromatography (IGC) and the static capsule technique. Inverse gas chromatography was used to investigate the solubility and diffusivity of several cosolvents in the photoresist polymer at ambient pressure. The static capsule technique was used to measure the solubility of CO_2 in the polymer at high pressures.

INVERSE GAS CHROMATOGRAPHY STUDIES

The IGC method was used to study how the solubility and diffusivity of cosolvents in the photoresist polymer can be changed by the presence of CO_2. The capillary column was coated with the polymer by the static coating technique.[1] The column was 35.5 m long and had a film thickness of 0.5 micron. To avoid the degradation of the polymer during the removal of residual monomer and solvent low temperature and low pressures were used, and in the preparation of the column the light source was a sodium vapor lamp. Capillary columns have such high volume to surface area ratios that the relative contribution of surface adsorption to the retention time is negligible above and below T_g.

Experimental data were collected at 75, 90, and 100°C for acetonitrile, propionitrile, and acetone. Some additional points at 90°C were measured for 2-butanone, benzonitrile, methyl-tert-butyl ether, and diethyl ethanol amine. The solvents were obtained from Aldrich Chemicals, St. Louis, MO (reagent grade, purity >99.5%). All data were at temperatures below the glass transition of the polymer.

Initially solubilities and diffusivities of the cosolvents were measured at the infinitely dilute limit using helium as the carrier gas. In each experiment, an elution curve (i.e., the solvent concentration at the end of the column) was obtained using a flame ionization detector. In the analysis of the experimental
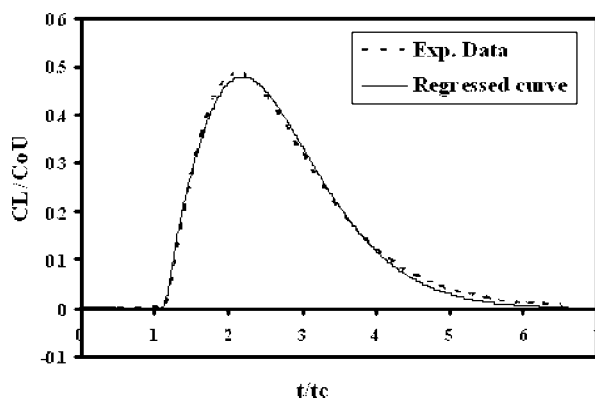
Figure 1 Propionitrile on photoresist column at 75°C.

data, the partition coefficient, K, and the diffusivity of cosolvents in the polymer, D_p, were regressed from a detailed model of the elution profile.[2,3] Example curves are shown in Figures 1 and 2. The dashed line indicates the measured dimensionless concentration of the solvent at the exit of the column. The solid lines represent the regression results. The two examples cover a highly soluble, low diffusivity case (propionitrile, Fig. 1), and a lower soluble, higher diffusivity case (acetonitrile, Fig. 2). There was excellent agreement between the theoretical model and the experimental elution profile in both cases.

The partition coefficients, K(He) in Table I, represent the concentration of solvent in the polymer (g/cm^3) divided by the concentration of the solvent in the gas phase (g/cm^3). Reproducibility was very good. All the results in the table are based on four duplicate experiments. The solubility of all the cosolvents decreased with increasing temperature. The diffusion coefficients for the solvents in the polymer, D_p(He) are given in Table II. As expected the diffusivity increased as the temperature increased.

Attempts to measure the solubility of CO_2 in the polymer using the conventional infinitely dilute IGC technique with helium as the carrier gas were not successful. The differences between the net retention times of the CO_2 and the noninteractive nitrogen were negligible. That is, the solubility of the CO_2 at atmospheric pressure and the infinitely dilute limit was below the capabilities of the IGC method.

To investigate the cosolvents solubility and diffusivity in the presence of CO_2, the carrier gas was changed to CO_2. The column was equilibrated with CO_2 at the selected temperature and then the measurements of the partition coefficients, K(CO_2) in Table I, and diffusion coefficients, D_p(CO_2) in Table II, were made. Experimental data were collected at 75, 90, and 100°C for acetonitrile, propionitrile, and acetone. An elution curve was obtained using the same velocity of the carrier gas and the same detector as in the experiments with helium.

The agreements between the theoretical model and the experimental elution profiles were good.

The solubility of all the cosolvents decreased with increasing temperature. The diffusivity increased as the temperature increased. The effects of CO_2 on the partition and diffusion coefficients of cosolvents in the polymer–solvent systems are depicted in Figures 3 and 4. In these figures the dashed line is the locus of points where there is no difference in the behavior of the cosolvents in CO_2 or helium. The solubility of all the cosolvents increased in the presence of CO_2. Although the solubility of CO_2 in the polymer is small, it apparently enhances the interactions between the polymer and cosolvent molecules. Spectroscopic studies have revealed the presence of a complex between poly(methyl methacrylate) and carbon dioxide.[4] The photoresist polymer, which has the same polymethacrylate backbone, could also form a complex with CO_2 that changes the interactions in the polymer–cosolvent systems. It is also possible that the presence of the cosolvents in the polymer enhanced the solubility of the CO_2. As mentioned earlier, however, the ambient pressure inverse gas chromatography technique cannot be used to investigate CO_2 solubility.

Figure 4 shows the expected increase in the diffusion coefficients in the presence of CO_2. Even the slight solubility of the CO_2 is enough to increase the free volume, and thus increase the diffusivity. The components with the higher solubility tend to provide a proportionately greater increase in the diffusivity.

To further investigate the reversibility of the influence of CO_2 on the solubility and diffusivity of the cosolvents, the carrier gas was switched back and forth between helium and CO_2. The column was equilibrated with each carrier gas for 48 h after each changeover. Consequently, there are results for five sequential experiments as shown in Figures 5 and 6: He-1, CO_2-1, He-2, CO_2-2, He-3. The most revealing results are summarized in Figure 5 for the solubility of the cosolvents in these five sequential experiments. In the first experiment with CO_2 as a carrier
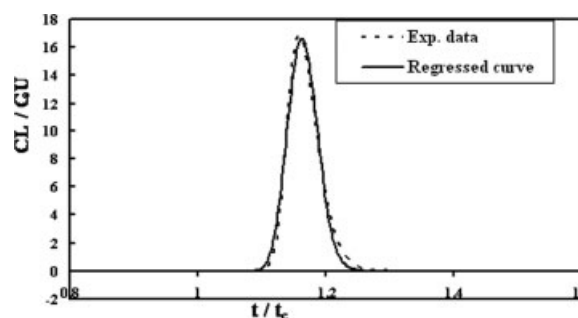

Figure 2 Acetonitrile on photoresist column at 100°C.

TABLE I
Solvent Partition Coefficients in the Photoresist–Copolymer Systems

Solvent	75°C		90°C		100°C	
	K(He)	$K(CO_2)$	K(He)	$K(CO_2)$	K(He)	$K(CO_2)$
Acetone	139.2	191.3	66.0	85.8	47.3	67.3
2-Butanone[a]			159.3			
Acetonitrile	210.7	235.5	100.9	108.8	70.6	81.6
Propionitrile	436.2	503.7	179.8	200.2	123.3	144.4
Benzonitrile[a]			10.4			
Methyl-tert-butyl ether[a]			0.63			
Diethyl ethanol amine[a]			242.0			

[a] These experiments were made after using CO_2 as the carrier gas and are referred to as He-2 data.

gas, there was a significant enhancement in the solubility of the cosolvents in the polymer. When the carrier gas was switched back to the helium (He-2), however, instead of the solubility going back to the original value, which was measured in helium (He-1), the solubility went up even more than in the CO_2-1 experiment. When the column was switched back to CO_2 as the carrier gas (CO_2-2) the solubilities returned to the values originally measured in the presence of CO_2. Finally, switching back to helium (He-3), the solubilities returned to essentially the same values which were measured in the He-2 experiments, that is, significantly higher then the first experiments with helium (He-1). This influence of CO_2 on the solubility of the cosolvents was unexpected. These observations are outside the range of the experimental error of this technique. Further discussion of this effect is presented in the next section.

The influence of CO_2 on the diffusivity of the cosolvents was not as clear as in the case of solubility. The presence of CO_2 is expected to plasticize the polymer (by increasing the free volume) and the diffusivities are expected to increase. For the first run with CO_2 as the carrier gas there was a significant increase in the diffusivities of acetone and propionitrile as shown in Figure 6. Returning to helium as the carrier gas (He-2) brought the diffusivities back to essentially their initial values. For the subsequent runs with CO_2 (CO_2-2) and helium (He-3) the differences were essentially within the scatter of the data. Essentially no variation in the diffusivity of the acetonitrile was observed as the carrier gas was changed. This suggests that for the smaller acetonitrile molecule the amount of free volume in the polymer is such that the additional free volume provided by the CO_2 has negligible effect on the diffusivity.

There are two purely speculative explanations for these results. There are studies in the literature that indicate that in glassy polymers, the swelling associated with the absorption of a gas such as CO_2 will persist for a short time after the CO_2 has been removed. That is, the CO_2 absorbs in the glassy polymers and increases its free volume. For at least a short time after the CO_2 is removed, however, the effects associated with the volume that the CO_2 occupied persists in the glassy state of polymer. In the previous studies, the influence of the presence of CO_2 on diffusion in glassy polystyrene was investigated, and the influence of the CO_2 appeared to persist for only a brief time, during which the glassy polystyrene relaxed to its original state.[5,6] It is possible that this polymer with its large bulky pendant groups relaxed more slowly, so that the effects introduced by the CO_2 persists in the polymer for a significant time after the CO_2 has been removed. This mechanism is consistent with the cosolvent solubility results. It was also consistent with the diffusivity results for propionitrile and acetone while, as stated

TABLE II
Solvent Diffusion Coefficients (cm²/s) in the Photoresist–Cosolvent systems

Solvent	75°C		90°C		100°C	
	D_p(He) $\times 10^{10}$	$D_p(CO_2) \times 10^{10}$	D_p(He) $\times 10^{10}$	$D_p(CO_2) \times 10^{10}$	D_p(He) $\times 10^{10}$	$D_p(CO_2) \times 10^{10}$
Acetone	0.0849	0.254	0.237	0.915	0.445	1.20
2-Butanone[a]			0.080			
Acetonitrile	1.85	2.75	4.54	5.70	7.30	7.72
Propionitrile	0.10	0.192	0.304	0.929	0.536	1.43
Benzonitrile[a]			97.9			
Methyl-tert-butyl ether[a]			10.9			
Diethyl ethanol amine[a]			0.242			

[a] These experiments were made after using CO_2 as the carrier gas and are referred to as He-2 data.
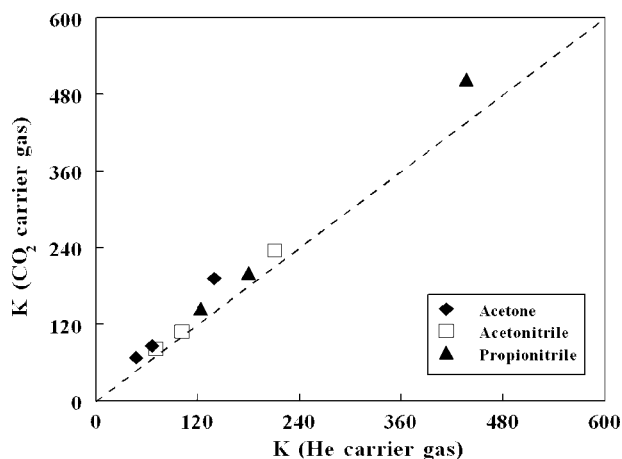
Figure 3 Comparison of CO_2 and helium on the partition coefficient of solvents in the photoresist polymer-solvent systems at 75, 90, and 100°C.

Figure 5 Effect CO_2 on the solubility of cosolvents in the photoresist-solvent systems at 90°C.

before, the diffusivity of the acetonitrile probably was not significantly affected because of its smaller molecular size.

The second possible interpretation of these results is that in the presence of CO_2 at 90°C, the polymer degraded and consequently it never returned to its original state or morphology. This explanation is not consistent, however, with the observed reversibility of the cosolvents solubility in helium.

STATIC CAPSULE ABSORPTION STUDIES

The solubility of CO_2 in the photoresist polymer was measured at 35°C and elevated pressures of CO_2 using the static capsule absorption technique. The details of the experimental protocol for this technique have been presented in the literature.[7] This
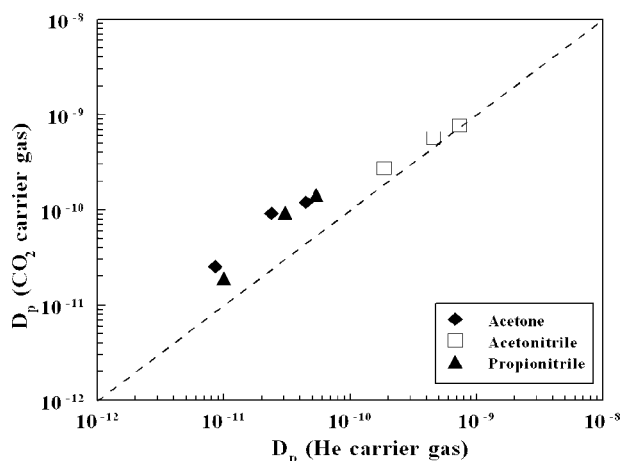
method does not provide diffusivity data. A sequential set of five CO_2 sorption runs was made. Specifications for all the runs are listed in Table III.

Run 1

- The capsule was degassed at 90°C for 40 h in a temperature controlled block and then cooled down to 35°C.
- CO_2 was admitted to the capsule at various pressures for about 24 h. Then the CO_2 source was disconnected, the capsule was weighed, and the solubility of CO_2 was calculated. The capsule was then put back into the temperature-controlled block, the lines to the capsule were evacuated, pressurized to the previous pressure, and allowed to sit for another 24 h to confirm that equilibrium had been reached.

Figure 4 Comparison of CO_2 and helium on the diffusion coefficient of solvents in the photoresist polymer-solvent systems at 75, 90, and 100°C.
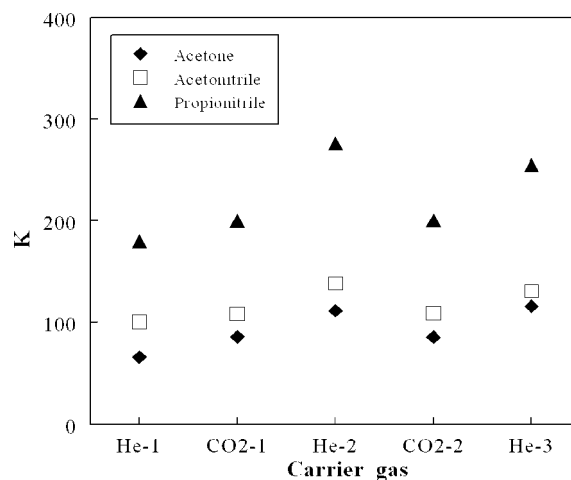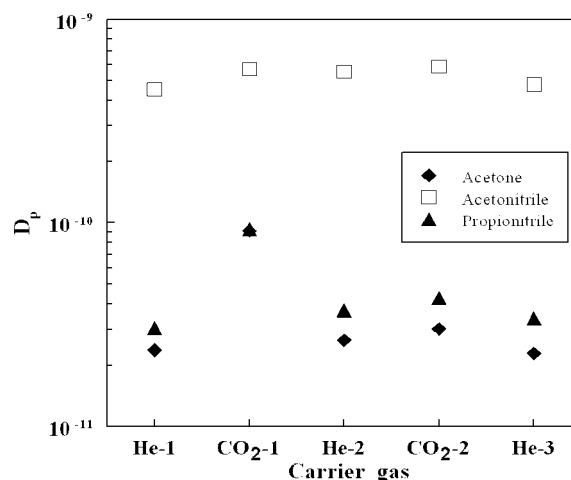

Figure 6 Effect CO_2 on the diffusivity of cosolvents in the photoresist-solvent systems at 90°C.

Runs 2 and 3

- To increase the reliability of the data the sample size was increased significantly for the subsequent runs as indicated in Table III. The capsule was degassed at 50°C for 60 h for Run 2 and for 50 h for Run 3 and then cooled down to 35°C.
- The CO_2 sorption was carried out as described for Run 1.

The densities of the CO_2 were calculated using the Benedict-Webb-Rubin equation of state.[8] The swelling effect of the photoresist polymer was estimated assuming ideal volume of mixing.

The sorption isotherms are shown in Figure 7. The second and third runs were in agreement; however, they both show that the solubilities of CO_2 in photoresist polymer doubled compared with the first run. This suggests that when the photoresist polymer was exposed to the high pressure CO_2 some free volume was created which remained in the unrelaxed glassy polymer after the CO_2 was removed. The reexposure of this metastable expanded polymer to the CO_2 results in an enhancement in the sorption. As shown in Figure 3 even low pressure exposure to CO_2 resulted in increased sorption. Although it was not completely clear what the mechanism associated with the exposure and then the degassing of the sample with CO_2 was, both the IGC and capsule experiments clearly indicated that the CO_2 absorption effect was nonreversible under some conditions. Either the absorption or desorption of the CO_2 was imparting a somewhat ''permanent'' excess free volume in the polymer or, alternatively, the presence of the CO_2 was in some way facilitating the degradation of the polymer. To further evaluate this theory, a run was made after annealing the polymer sample.

Run 4

- The sample was maintained at a temperature of 115°C for 5 days.
- The degassed sample was again exposed to CO_2 at 35°C and the sorption was determined as before. However the maximum pressure was 2741 kPa rather than the 4222 kPa as in Run 1.

TABLE III
Experimental Conditions for the Static Capsule Absorption Measurements

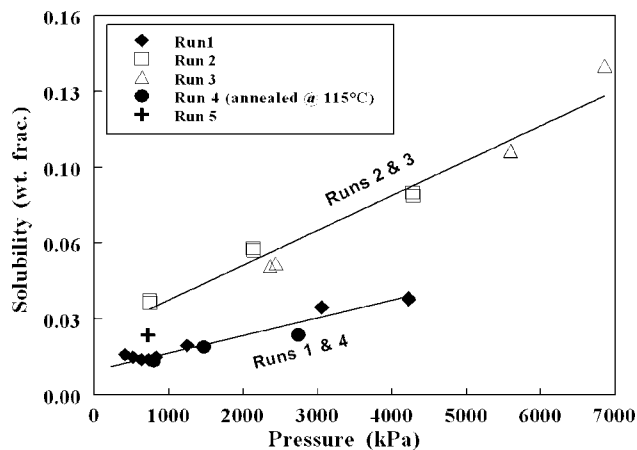|	Run 1	Run 2–5
Weight of dry polymer (g)	0.50507	0.89175
Volume of the capsule (cm^3)	12.21	12.21
Volume of tray (cm^3)	0.50	0.97
Volume of headspace before taking into account the swelling (cm^3)	11.30	10.51

Figure 7 Photoresist-CO_2 sorption isotherms at 35°C. Runs 1–3 were performed in succession after receiving the photoresist sample. Run 4 was performed after a high temperature annealing, whereas Run 5 followed a 35°C degassing.

If nonequilibrium free volume was causing the solubility enhancement, then the fully relaxed sample should exhibit the same sorption behavior as observed in the first CO_2 run. The solubility did indeed drop down to the level observed in the first run. The next run was performed to see if the nonreversible sorption effect could be repeated.

Run 5

- The sample was degassed at 35°C for 10 h.
- The degassed sample was again exposed to CO_2 at 35°C and the sorption was determined as before.

The result did show a noticeable rise in CO_2 solubility, but not to the levels observed in Runs 2 and 3 where the sample had previously been exposed to a higher pressure of CO_2. Since the maximum pressure reached in Run 4 was less than that in Run 1, leading to less excess free volume was created. Thus, there was clear evidence that pulsing CO_2 into unrelaxed photoresist polymer could greatly enhance solubility. The amount of excess free volume in the sample, however, is a complex function of the sample's history, and the resulting enhancement in solubility is difficult to reproduce. Figure 7 shows that extrapolation of the sorption isotherm to zero pressure will not go through the origin, but this is not uncommon for sorption behavior in glassy polymers. As shown by Chiou and Paul[9] there is often nonlinear behavior at the lower pressures with the linear portion occurring as the pressure increases.

CONCLUSIONS

The objective of this effort was to determine the effects of CO_2 on the properties of a typical photo-

resist material, in particular to see how it might plasticize the material and affect the removal of polymer coatings and the diffusion and solubility of cosolvents in the polymer. The results show that CO_2 affects the solubility of cosolvents even at low pressures where the solubility of the CO_2 is so small that it has no discernible effects on the diffusivities of the solvents. Clear indications were found that the effects of the CO_2 on the photoresist persisted for an extended time after the CO_2 was removed. In the ambient pressure IGC experiments the solubilities of cosolvents were higher after exposure to CO_2. In the capsule experiments large increases in the solubility of the CO_2 were observed after the photoresist was exposed to high pressure CO_2. This was evidence that pulsing CO_2 unto the unrelaxed polymer can greatly enhance the solubility.

It was obvious from these studies that some unusual nonreversible effects were associated with the absorption and desorption of CO_2. The best way to elucidate this phenomenon would be to conduct similar studies with other bulky structure polymers. If absorption and desorption of CO_2 and polymers show similar irreversible affects on the solubility and diffusivities of cosolvents at temperatures below the glass transition, this would be a clear indication of the ability of absorbed CO_2 to introduce free volume in a glassy polymer which persists after the CO_2 is removed.

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