Compressed Fluid Technology: Application to RIE-Developed Resists

A novel plasma-developed resist lithographic process is described that uses compressed CO_2 to extract nonvolatile siloxane molecules from host organic polymers. The process is capable of at least 0.75 μm resolution with an X-ray sensitive guest siloxane-host polymer system. A processing window was investigated and defined to eliminate or minimize film damage during compressed fluid extraction. Polymer deformation was usually avoided by using supercritical CO_2 rather than liquid CO_2, provided that film thicknesses were ≤ 1 μm. Increased solute concentrations in the host polymer also adversely affected the quality of extracted films. An *in situ* capacitance process monitoring scheme was developed which indicated that film damage, when observed, was primarily caused by explosive decompression of the solvent from the host polymer.

D. H. Ziger
AT&T Engineering Research Center
Princeton, NJ 08540

T. M. Wolf, G. N. Taylor
AT&T Bell Laboratories
Murray Hill, NJ 07974

Introduction

Supercritical fluid extraction (SCFE) processes use compressed fluids above their respective critical points as ordinary chemical solvents. The advantages derived from using SCFE technology rather than ordinary liquid extraction methods arise because compressed fluids are good solvents only under pressure at liquid or liquidlike densities. Consequently, components of a mixture that are soluble in a supercritical fluid may be extracted and the pregnant solvent may be cleanly unloaded downstream of the process by decompressing the solvent to a gaslike density. Similarly, the compressed solvent is completely removed from the extracted residue by decompressing the system. Solvent contamination of the extract and residue is avoided and subsequent energy intensive distillation or drying processes are unnecessary. Carbon dioxide is the most widely used supercritical fluid because it has a readily accessible critical temperature (31.1°C), is nonpoisonous, and is inexpensive. Applications of SCFE that exploit these advantages have been proposed and implemented in such diverse areas as the food, petroleum, and pharmaceutical industries (Paulaitis *et al.*, 1983).

We have investigated a novel application of SCFE that uses compressed fluids to extract nonvolatile siloxane molecules from 1 μm thick organic polymer films. This application, in the area of microlithography, poses severe restraints on the SCFE process:

1. Extraction must be complete and uniform
2. Polymer deformations due to extraction must be ≤ 0.1 μm to resolve submicron features
3. Total processing time (compression, extraction, decompression) must be minimized

(For a review of microlithographic techniques, exposure apparatus, lithographic materials, and pattern transfer processes, see Thompson et al., 1983, 1984.)

Plasma-developed resist (PDR) processing

In this work, SCFE was investigated as an alternative to a thermal stripping (fixing) process needed to remove unreacted siloxane compounds dissolved in an organic polymer matrix. The overall lithography scheme, first reported by Taylor *et al.* (1981) was designed to pattern submicron features in thin organic films (≤ 1 μm). Figure 1 illustrates the standard process in which an organometallic reactive monomer *rm* undergoes homopolymerization or addition to the host polymer *P* upon exposure to various types of radiation. After exposure, unreacted monomer is removed with a forced hot-air fixing process. Once free monomer has been removed, patterns can be developed using O_2 reactive ion etching (RIE). Metal-free, unexposed areas are removed via oxidative stripping, Eq 1, while metal-containing imaged areas are protected by the formation of a nonvolatile metal oxide film Eq. 2:

$$\text{Unexposed Regions:} \quad P + O_2 \rightarrow CO_2 + CO + H_2O \qquad (1)$$

Exposed Regions:

$$\text{Organic Siloxane} + O_2 \rightarrow SiO_x + CO_2 + CO + H_2O \qquad (2)$$

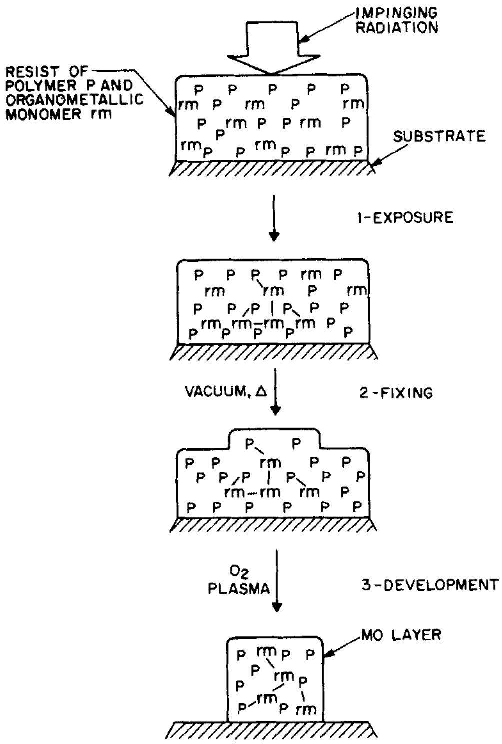

Figure 1. Plasma-developed resist scheme.

where *P* is a polymer having carbon, hydrogen, and oxygen atoms. The most successful of these plasma-developed resists is a mixture of *bis*-(4-acryloxybutyl)tetramethyldisiloxane, BABTDS, in poly(2,3-dichloro-1-propyl acrylate), DCPA. Using this mixture, 0.5 μm lines and spaces have been resolved using X-ray radiation. However the developed thickness is less than half the initial film thickness, thus limiting its use to a trilevel process (Moran and Maydan, 1979) since there is insufficient resist after development to serve as an effective etch mask for underlying substrate layers. Thus far, the limitation of this or any other organometallic-based plasma-developed resist system is the failure to achieve differential etch rate ratios of exposed to unexposed resist of greater than 5:1.

Enhancing the PDR scheme

Intuitively, the etch rate ratio should be considerably improved by the use of higher percentages of organometallic reactants containing a higher proportion of Si-O groups in organic polymer hosts. This may be accomplished by using organometallic polymers and oligomers having high metal content. These cannot be removed by thermal fixing even at high vacuum. On the other hand, such reagents would have better thermal stability and would resist inadvertent outgassing during prebake. Compatibility for siloxanes dissolved in host organic polymers is expected to be a severe constraint for siloxane polymers but should be a less serious problem for oligomers.

Solvent fixing is an obvious alternative to thermal fixing of nonvolatile siloxane-polymer mixtures. In the simplest application, a liquid solvent that interacts minimally with the host polymer is chosen to extract the solute. The solvent must be chosen to minimally swell the polymer host and to readily dissolve the organometallic solute. Ideally, the solvent penetrates the host polymer by diffusion; there it dissolves and dilutes the organosilicon solute and carries the solute to the surface where it may be removed by the bulk liquid. However, our initial experiments using cyclohexane to extract BABTDS from DCPA were not very promising due to the formation of surface rippling distortions that were frequently observed on extracted films. These reticulations, which were probably caused by slight solvent swelling of the host polymer, were transferred to the wafer surface during oxygen RIE and distorted the developed patterns, which exhibited submicron resolution in undistorted regions. While it might be possible to minimize or perhaps eliminate these distortions for a particular host polymer by optimizing the solvent, each solute-host polymer system would require its own solvent and the trial and error experimentation required to obtain it.

To avoid the problems that we found using liquid extractive fixing, we propose using supercritical fluids or compressed liquids to remove free siloxane monomer present in the unpatterned regions. These compressed solvents will not dissolve crosslinked polymers but will penetrate them under a pressure gradient. Compressed CO_2 is a natural choice for removing residual siloxane monomers from resists. Supercritical CO_2 is an excellent solvent for siloxanes (McHugh and Krokonis, 1986) and has been successfully used to extract cyclic siloxanes from thermally cured RTV films (Ziger, unpublished results). Furthermore, CO_2 processing can be done at moderate temperatures avoiding thermally induced polymer flow or additional polymerization of unreacted monomer, which can occur during high-temperature fixing (Taylor *et al.*, 1983). Lastly, there is complete solvent removel from the film after depressurization.

Experimental Method

Chemicals

PDXR-2 is an acronym for plasma-developed X-ray resist. It is 92.5% poly(2,3-dichloro-1-propyl acrylate), DCPA, and 7.5% *bis*-(4-acryloxybutyl)tetramethyldisiloxane, BABTDS, at 11 wt. % solids in chlorobenzene. Poly(chloromethylstyrene), PCMS, was obtained from R. Tarascon (Tarascon et al., 1984).

Siloxane compounds for these extraction experiments were chosen on the basis of compatibility with potential host polymers and high silicon content. Tetramethyltetravinylcyclotetrasiloxane, TMTVCTS, *tris*-(chloromethyldimethylsiloxy)-methacryloxypropylsilane, TCMMA, PSX653, and PSX654 were all obtained from Petrarch Systems, Inc. (Bristol, PA.). PSX653 is poly(chloromethylmethyl siloxane) end-capped with chloromethyldimethylsilyl chloride. It had $\overline{M}_w = 2{,}560$ and $P = 1.97$. PSX654, which is the reaction product of PSX653 with potassium acrylate, contained 46 mol % acryloxymethyl and 54 mol % chloromethyl functionality and had $\overline{M}_w = 1{,}540$ and $P = 1.46$. TCMMA was purified by eluting a 10% solution of the crude TCMMA in a 95/5 mixture by volume of hexane and ethyl acetate through a column of packed silica gel.

Bis-(4-azidophenyl)ether, BADE, was prepared from the corresponding amino compound using the general procedure of Mallory (1963). The polymers used in the SCFE studies of BADE removal were obtained from commercial sources and were used as supplied.

Apparatus

Lithography Equipment. Deep ultraviolet (DUV) exposures were done with an Optical Associates Inc. model 25 DUV source equipped with 260 nm optics. X-ray exposures were made with a $Pd_{L\alpha}$ exposure system that has been described previously. A Perkin-Elmer (Norwalk, CT) model 330 UV spectrometer was used for DUV measurements. Exposed and extracted wafers were developed using a Cooke Vacuum Products (Norwalk, CT) reactive ion etcher. Typical etching conditions were 10–20 sccm O_2, 20 mtorr, 20 W, and -200 V bias.

Extraction Equipment and Procedure. The organization of the wafer extraction apparatus is shown in Figure 2a. A Haskel (Burbank, CA) air-driven compressor (AGD-62) pressurized the source gas to a high-pressure reservoir. Downstream pressure was controlled with a Tescom 1024 series regulator. The wafer extraction vessel was a modified 1 L, 3 in. (76 mm) ID autoclave (Autoclave Engineers, Erie, PA.) whose volume was plugged with either an aluminum or a Teflon insert leaving a 1/8 in. (3 mm) gap between the plug and body cover.

Extractions of thin films by SCFE were done by the following general procedure: Typically a 3 in. (76 mm) dia. Si wafer was spin-coated with resist baked in a forced air oven and then placed in the vessel, which was sealed and compressed to the desired pressure through the inlet ports. Backfilling was used to avoid damaging the film surface during pressurization and the throttled gas was heated to prevent dry ice formation in the inlet stream. After pressurization, flow was switched to the center of the cover through which the solvent flowed for a measured time. The CO_2 was vented to atmospheric pressure through a heated micrometering valve. After exiting the vessel, its volume at ambient pressure was measured using a dry test meter. After the allotted time, the CO_2 supply was shut off and the system was allowed to vent to atmospheric pressure. Pressurization and decompression were generally done as quickly as possible, although decompression time varied substantially from run to run depending upon both the density and the volume of gas in the extraction vessel. The entire extraction cycle could generally be completed in 4–5 min using a typical 2 min flow period.

Extraction Conditions. A partial phase diagram for CO_2 is shown in Figure 3. Carbon dioxide was used in both its liquid ($T < 31.1$°C, $P \geq P_T^{sat}$) and supercritical ($T > 31.1$°C, $P > 72.8$ bar) states. Typical extraction conditions were 35–40°C and 100 bar. Under these SCFE conditions, the density of CO_2 varied from 0.7–0.8 g/cm^3.

Temperature and pressure in the bulk solvent were measured with thermocouples and a strain gauge, respectively, which in turn were monitored with an HP-85 computer. A typical extraction cycle is shown in Figure 4. Pressurizing in the manner described above caused the temperature to increase temporarily while decompression lowered the temperature. Consequently, temperature could not be closely controlled during pressurization and decompression although it was reasonably stable during the actual extraction process.

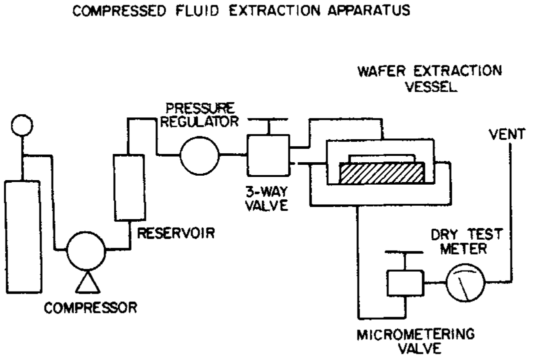

Figure 2a. Compressed fluid extraction apparatus.

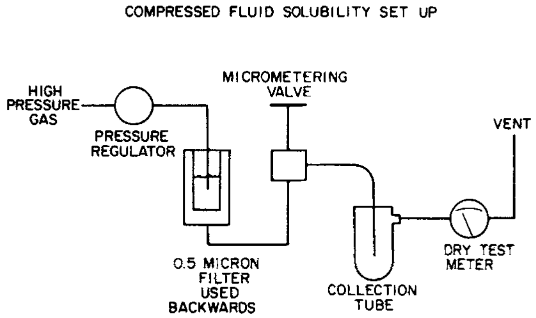

Figure 2b. Compressed fluid solubility apparatus.

Solubility Measurements. Solubility data for two siloxanes, TMTVCTS and TCMMA, were measured in liquid CO_2 using a flow technique described by Johnston et al. (1981). These data were used to roughly gauge the relative solubility of these siloxanes in compressed CO_2. The apparatus for these measurements is shown in Figure 2b. Compressed fluid of measured volume was brought in intimate contact with ≈ 1 g solute and the mass of solute volatilized by the solvent was collected in a cold trap and weighed. A 0.5 μm filter was used to hold the solute, and initial pressurization was done by backfilling to minimize solute loss due to entrainment.

Results

Solubility measurements

The solubility of TMTVCS and TCMMA dissolved in liquid CO_2 at 20°C and 100 bar were approximately 7.5 and 0.8 wt. %, respectively. Assuming that a 1 μm film weighs 0.005 g, these solutes could potentially be extracted from host polymers with

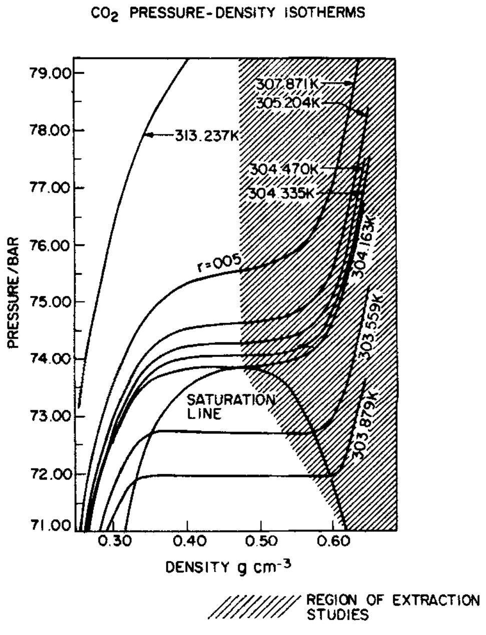

Figure 3. Partial phase diagram for carbon dioxide.

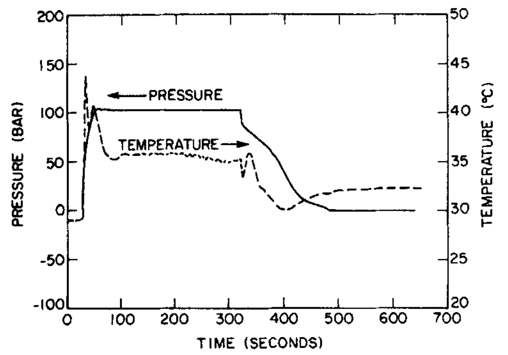

Figure 4. Time-temperature-pressure SCFE conditions.

milligrams of liquid solvent provided that the mass transfer is adequate. For comparison, a 2 min extraction process using CO_2 venting to the atmosphere at 3 L/min flows about 5 g of solvent over the thin film. Solubility of these solutes in supercritical CO_2 is expected to be of the same order of magnitude since the densities of supercritical and liquid CO_2 states are similar. Consequently, incomplete removal of TMTVCS and TCMMA from host polymers using 5 g of solvent should be attributed to mass transfer limitations in the absence of strong host polymer-solute interactions. Finally, these data suggest that less volatile siloxane compounds also can be removed using the above extraction conditions since resulting CO_2 mixtures of TMTVCS and TCMMA are undersaturated by three orders of magnitude.

Extraction of azides

The ability of supercritical or compressed liquid CO_2 to permeate a thin polymer film and extract a monomeric or oligomeric species may be restricted by the physical properties of the polymer. To test this hypothesis, we investigated the ability of compressed liquid CO_2 to extract *bis*-(4-azidophenyl)ether, BADE, from a series of polymer films that varied in polarity and phase. Table 1 summarizes results from these extraction experiments. Such azides are useful in obtaining high-resolution patterns using gas-phase functionalization reactions of the type described by Wolf et al. (1984). The effectiveness of the extraction method could be monitored by looking at the disappearance of BADE initially present in the films spectroscopically at 265 nm in the UV, as seen in Figure 5. This series of experiments showed that compressed CO_2 processing removed a minimum of 90% of the BADE from all films except poly(4-hydroxystyrene), a highly polar and glassy polymer. Evidence for complete removal of BADE may be hidden by the varying baseline found while conducting the spectroscopy experiments. Thus, we have established a guide for the type of polymer that can be considered for extractive fixing using supercritical or compressed liquid extraction. With the exception of highly polar and glassy polymers, we could expect to remove materials from thin films solely on the ability of the fluid to solvate the monomer or oligomer and then undergo a successful mass transport.

Table 1. CO_2 Extraction of BADE-Polymer Mixtures*

			Absorbance at 265nm	
Polymer†	T_g °C	Polarity	Before Extraction	After Extraction**
c-PIP	<25	low	1.06	0.10
PVC	80	low	1.26	0.08
PEA-GMA	46	moderate	0.81	0.07
PAMA-HMA	−55	moderate	1.26	0.11
PMPS	100	low	1.46	0.02
PMMA	105	moderate	1.02	0.02
PHS	>80	high	2.10	2.00

*Approx. 1 μm thin films containing 10% BADE, *bis*-(4-azidophenyl)ether, dissolved in each host polymer

**Extraction conditions: 2 min using liquid CO_2.

†PMPS, poly(methylpentenesulfone); PVC, poly(vinyl chloride); PMMA, poly(methyl methacrylate); c-PIP, cyclized polyisoprene; PEA-GMA, poly(ethyl acrylate-co-glycidyl methacrylate); PAMA-HMA, poly(allyl methacrylate-co-hydroxyethyl methacrylate); PHS, poly(4-hydroxystyrene).

SCFE experiments with plasma-developed resist systems

SCFE-Fixed PDXR-2 Lithography. The first system investigated was BABTDS in DCPA, which was patterned on wafers by X-ray lithography according to methods already described. The results from these experiments indicate that BABTDS is rapidly removed in liquid carbon dioxide. Fine line, 0.75 μm, patterns were completely extracted using 1 min of liquid CO_2 flowing at 3 L/min. The CO_2-fixed samples compared favorably with the thermally fixed wafers. Scanning electron micrographs showing this comparison are presented in Figure 6. Swelling was not observed for the SCFE-processed wafer and the extraction did not introduce inhomogenities into the host polymer. It is believed from previous experimental work with this system that thermal fixing might show considerable limitations for finer lines (0.3–0.5 μm) due to thermally induced polymerization.

SCFE-Fixed PDR with Heavy Siloxanes. The results described in the preceding section, combined with past experience, suggested that much higher molecular weight siloxanes should be removed easily from organic thin films. Polydimethylsiloxane

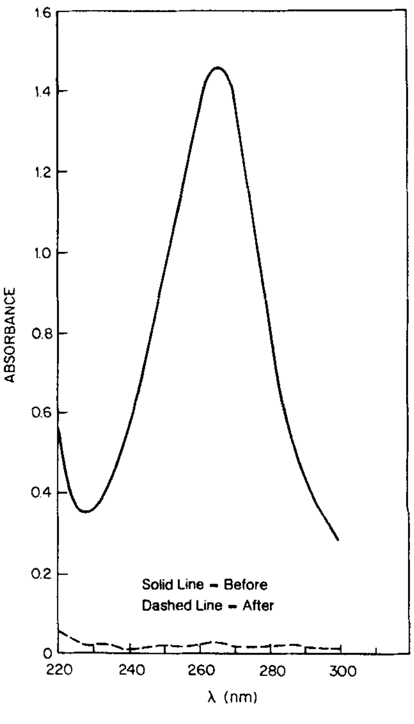

Figure 5. Extraction of *bis*-(4-azidophenyl)ether from poly(methylpentenesulfone).

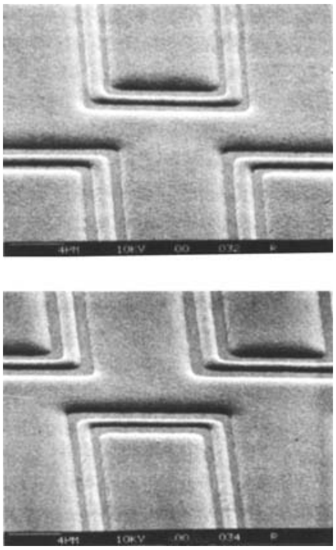

Figure 6. SEM micrographs comparing PDXR-2 fixing.
Top, thermal fixing
Bottom, SCFE fixing

(PDMS) oligomers appeared to be a good starting point due to their excellent oxygen RIE resistance and good solubility in CO_2. Unfortunately, PDMS oligomers are very incompatible with many organic host polymers, and spun films phase-separated as the solvent evaporated. Several deep UV (DUV) and X-ray sensitive systems containing other oligomeric siloxane reagents appeared macroscopically homogeneous and could be locked into a suitable host organic polymer upon exposure to radiation.

After exposure, wafers were extracted to remove unlocked siloxane. The ability to strip these siloxane oligomers from compatible host polymers was reflected in O_2 reactive ion etching rates of extracted unpatterned regions compared to pure host polymers. Table 2 shows that extracted unexposed regions etched at similar rates to the pure unextracted host polymers. This indicates that virtually all free siloxane was removed during SCFE.

Lithographically, resist properties such as resolution and etching resistance were dependent on the host polymer. We observed excellent etching resistance when heavy siloxanes were incorporated into a rubbery host such as DCPA (T_g = 18°C, Taylor et al., 1977), but we could not define features smaller than 5 μm by either X-ray or photochemical exposure.

Examination of Figure 7 provides an insight into the observed competitive processes. We have plotted etch rate vs. percentage of PSX653 in a glassy host polymer (PMMA) and a rubbery host (DCPA). None of the samples was irradiated or SCFE-fixed. It is unlikely that 5 wt. % PSX653, homogeneously distributed in DCPA, has sufficient silicon content to reduce O_2 RIE by about a factor of 20. Consequently, we hypothesize that the dramatic decrease in etch rate for 5 wt. % PSX653 in DCPA must be attributed to the ability of the siloxane to migrate in the rubbery host polymer matrix and eventually concentrate at the film's surface before or during RIE. Additionally, rubbery host polymer systems using heavy siloxanes were frequently pitted after O_2 RIE, implying that phase separation had taken place at the film's surface. Silicon-rich microdomains did not etch, while silicon-depleted areas were etched deeply into the film yielding a "Swiss cheese" appearance. A more rigid matrix such as PMMA retards the movement of the siloxane in the film and we observed neither phase separation nor substantial reduction in etching at low siloxane film concentrations, Figure 7.

Table 2. Extraction Effects on RIE Etching Rate for DCPA-TCMMA Mixtures

TCMMA %	RIE Etching Rate, μm/min Before Extraction	RIE Etching Rate, μm/min After Extraction
0	0.14	
7.5	0.06	0.15
15	0.06	0.16

*Extraction conditions: 2 min exposure to flowing supercritical fluid CO_2

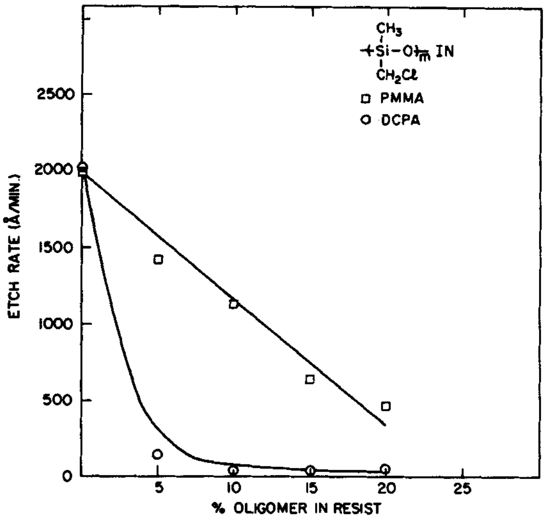

Figure 7. Etching rate as a function of siloxane content.

DUV exposure of an acrylated siloxane, PSX654, dissolved in glassy poly(chloromethylstyrene), PCMS, (T_g = 85°C, Choong and Khan, 1983) further illustrated the dependence of these systems upon T_g. Since 50% of the repeat units in PSX654 are acrylate moieties, we expected DUV radiation to extensively crosslink and graft this oligomer onto the backbone of PCMS. However, even for this system the developed thickness after SCFE fixing and O_2 RIE etching was less than 50% of the initial thickness. This implies that the acrylated siloxane was not effectively locked onto the host polymer. Generally, lithographic systems using heavy siloxanes in glassy host polymers yielded submicron resolution but poor RIE etch resistance.

Experiments with PMMA and TCMMA in the presence of a photoinitiator may illustrate the processes occurring in the films during exposure and SCFE. TCMMA is a monomethacrylate and should give a linear polymer with no branching when free radical polymerization occurs. Films consisting of 20 wt. % TCMMA in PMMA were spun and DUV exposed using a resolution pattern mask. Approximately 5 wt. % Irgacure 651 (Ciba-Geigy, Ardsley, NY) was added to promote siloxane grafting onto the host polymer backbone and oligomerization via free radical mechanisms. These films were then fixed at various CO_2 densities to extract unlocked siloxane oligomer. Since

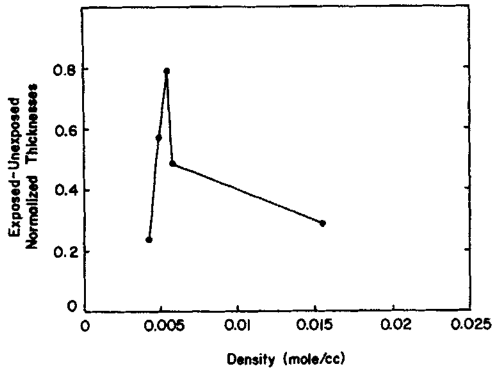

Figure 8. Effect of CO_2 solvent density on exposed-unexposed film thicknesses.

the solvating power of a supercritical fluid solvent is related to its density (Ziger and Eckert, 1983), fixing as a function of solvent density discriminated between TCMMA in the unexposed regions and various TCMMA photoproducts in the exposed areas. After compressed fluid fixing, these films were etched by O_2 RIE and the difference in normalized developed thicknesses of the exposed and unexposed areas, $NT_{DE} - NT_{DU}$, was measured. Figure 8 shows a plot of this difference in normalized thickness as a function of extraction density. At low densities, neither the exposed nor unexposed areas etched to the substrate, implying that little siloxane was removed from either area. However, as the extraction density increased, the unexposed regions etched faster then the exposed areas. Evidently, at these densities siloxane was removed only from the unexposed regions. A maximum in the difference of normalized thicknesses was found near 0.06 mol/cm^3 above which the exposed regions began etching at comparable rates to unexposed areas. Apparently, at high CO_2 fixing densities the solvent extracted oligomerized TCMMA from the exposed areas, leading to poor RIE etching resistance. Also, since siloxane could be extracted from the exposed regions for samples fixed at high CO_2 densities, this indicates that little grafting occurred on the host polymer. Unfortunately, submicron resolution was obtained only for films fixed at high CO_2 densities. Moderate fixing densities left residual siloxane in the unexposed areas, severely limiting resolution.

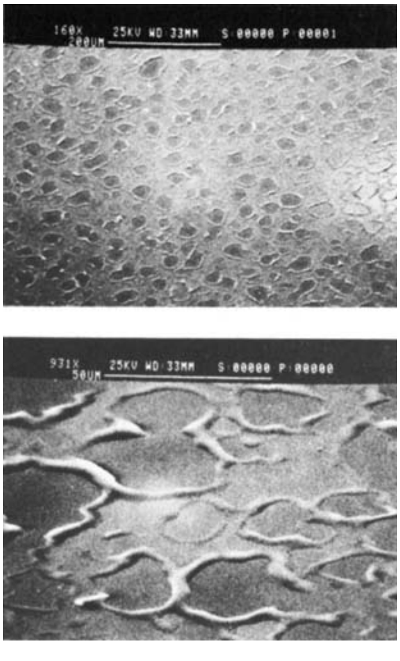

Figure 9. SEM micrographs of extraction-induced crazing of PCMS with liquid CO_2.

We believe that this behavior is analogous to the PCMS-PSX654 system where oligomerization is occurring with a small amount of grafting. Unreacted PSX654 and its higher molecular weight oligomers were removed by SCFE, resulting in low normalized thicknesses in the exposed areas. Replacing PCMS with DCPA (the rubbery host) shows a dramatic decrease in the etch rates for films containing PSX654 or TCMMA that have been photoexposed, fixed with SCFE, and etched. We attribute our failure to define features <5 μm in DCPA to the high degree of polymerization in rubbery host polymers during exposure. The high rate of propagation and increased mobility of active sites in these rubbery hosts affected polymerization beyond the exposed/unexposed interface to a distance of 2.5 μm, thereby minimizing pattern definition to 5 μm and larger.

Extraction-induced polymer deformation

Host polymer films were deformed during compressed fluid fixing when the extraction was done under certain conditions. Figure 9 shows a scanning electron micrograph of a PCMS film deformed by a liquid CO_2 and indicates that the extraction could severely blister the host polymer film. Polymer deformation was most likely to occur if one or more of the following conditions occurred during the extraction process:

1. $T < 31.1$°C during the extraction cycle
2. Thick host polymer films (>1.5 μm)
3. High solute concentrations
4. Glassy rather than rubbery host polymers

The above observations indicate that polymer deformation occurred during decompression. Upon decompression, liquid CO_2 must undergo a liquid to vapor phase transition. At the saturation vapor pressure (see the CO_2 phase diagram, Figure 3) the liquid will boil on the film surface, a process that could cause surface deformations. Moreover, if the solvent diffusion rate is slow, the CO_2 will become supersaturated within the film, which could eventually lead to defects due to bubble formation within

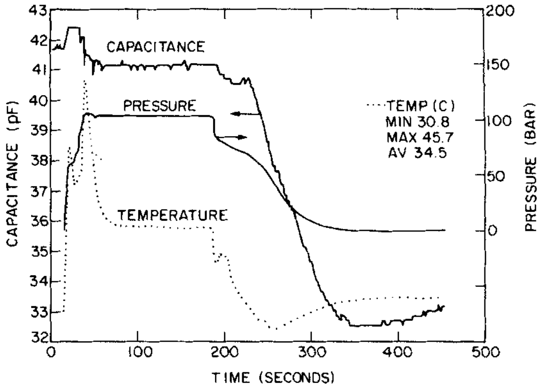

Figure 10. *In situ* capacitance measurements of 10 μm film processed with liquid CO_2.

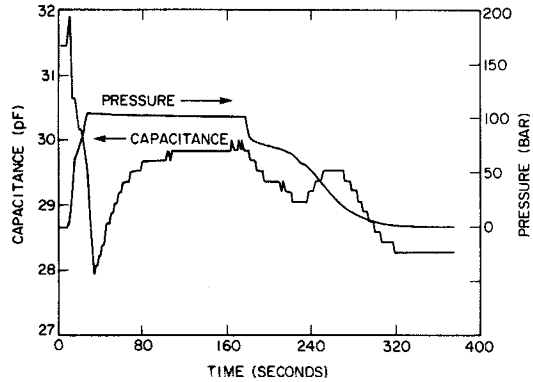

Figure 11. Coated triple-track capacitance measurement during extraction.

the host polymer. Supersaturation should be worse for thicker films, as the amount of dissolved CO_2 is increased along with overall resistance to diffusion.

The effect of solute concentration in the host polymer would be to increase the solubility of CO_2 in the film since CO_2 and siloxanes are mutually soluble at low concentrations of one in the other. This entraining effect could possibly supersaturate films even in the exposed areas after most of the solute has been extracted, which may increase the possibility of bubble nucleation leading to extraction-induced defect formation. Finally, very high solute concentrations could increase the solvent concentration to such an extent that the host polymer is irreversibly strained.

Capacitance measurements of films under pressure were done to study the mechanics of supercritical fluid extraction, liquid extraction, and extraction-induced defect formation. Triple-track testing chips, which are normally used for dielectric materials testing (Iannuzzi, 1981), were coated with pure polymers and polymer-solute mixtures. Differences in capacitance between meander patterns of exposed aluminum lines at a set frequency (1 kHz) caused by the extraction process reflected a change in the dielectric constant of the host polymer, its thickness or a combination of both effects. (Further details of this technique and results may be found in Ziger, 1987.) Defects induced by SCFE substantially decreased the capacitance that was generally seen during decompression. The effect of SCFE CO_2 treatment on a thick (>10 μm) DCPA film is shown in Figure 10. Loss in capacitance occurred during decompression and the processed film was severely pitted. Extraction of solutes from host polymers could be monitored by measuring capacitance vs. time and pressure at a set frequency, Figure 11. For rubbers, the capacitance generally decreases sharply during pressurization, implying that the CO_2 first swells the film, degrading the dielectric integrity of the host polymer. The capacitance then slowly increases as the film is extracted, possibly because swelling has been reduced due to lower presumed CO_2 solubility in the extracted film.

Conclusions

We have investigated the use of liquid and supercritical fluid CO_2 to extract siloxane compounds from 1 μm thick organic films for use in a microlithography process. A processing window was defined that provided at least 0.75 μm resolution using supercritical CO_2 fixing for an X-ray exposed lithography system known as PDXR-2. Lithography results using heavy siloxane oligomers were dependent on the nature of the host polymer. Generally, glassy host polymers yielded better resolution than rubbery polymers, but thinner films after O_2 development. Capacitance measurements were used to monitor extraction phenonmena *in situ*. These measurements showed that decompression was the most likely cause of film damage during SCFE fixing.

This technique is still in the research stage and its applicability to microlithographic fabrication in a production environment is presently unknown.

Acknowledgment

The authors acknowledge comments E. J. Kramer regarding film damage during compressed fluid extraction.

Literature cited

Choong, H. S., and F. J. Khan, "Poly(chloromethylstyrene): A High-Performance X-Ray Resist," *J. Vac. Sci. Technol.*, **B1**, 1066 (1983).
Iannuzzi, M. M. "Development and Evaluation of a Preencapsulation Cleaning Process to Improve Reliability of HICS with Aluminum Metallized Chips," *IEEE Trans*, **CHMT-4**, 429 (1981).
Johnston, K. P., D. H. Ziger, and C. A. Eckert. "Solubilities of Hydrocarbon Solids in Supercritical Fluids—The Augmented Van der Waals Treatment," *Ind. Eng. Chem. Fundam.*, **21**, 191 (1981).
Mallory, F. B., *Org. Syn. Col.*, **IV**, 74 (1963).
McHugh, W. A., and V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, Butterworths, Boston (1986).
Moran, J. M., and D. Maydan, "High-Resolution, Steep-Profile Resist Patterns," *Bell System Tech.*, **58**, 1027 (1979).
Paulaitis, M. E., J. M. Penninger, R. D. Gray, and P. Davidson, eds., *Chemical Engineering at Supercritical Conditions*, Ann Arbor Sci., Ann Arbor, MI (1983).
Tarascon, R. G., M. A. Hartney, and M. J. Bowden, in *Radiation Sensitive Polymers*, L. F. Thomposon, C. G. Willson, J. M. Frechet, eds., *Am. Chem. Soc. Symp. Ser.*, **266**, Washington, DC (1984).
Taylor, G. N., G. A. Coquin, and S. R. Somekh, "Sensitive Chlorine-Containing Resists for X-Ray Lithography," *Polym. Eng. Sci.*, **17**, 420 (1977).
Taylor, G. N., T. M. Wolf, and J. M. Moran, "Organo-Silicon Monomers for Plasma-Developed X-Ray Resists," *J. Vac. Sci. Technol.*, **19**, 872 (1981).
Taylor, G. N., M. Y. Hellman, M. D. Feather, and W. E. Willenbrock, "Evaluation of the Influence of Process Factors on Plasma-Developed X-Ray Resist Properties," *Polym. Eng. Sci.*, **23**, 1029 (1983).
Thompson, L. F., C. G. Willson, and M. J. Bowden, eds., *Introduction to Microlithography, Am. Chem Soc. Symp. Ser.*, **219**, Washington, DC (1983).
Wolf, T. M., G. N. Taylor, T. Venkatesan, and R. T. Kraetsch, "The Scope and Mechanism of New Positive Tone Gas-Phase Functionalized Plasma-Developed Resists," *J. Electrochem. Soc.*, **131**, 1164 (1984).
Ziger, D. H., "*In situ* Capacitance Monitoring of Thin Polymer Films During Compressed Fluid Extraction," *J. Matls. Res.*, in press (1987).
Ziger, D. H., and C. A. Eckert, "Correlation and Prediction of Solid-Supercritical Fluid Phase Equilibria," *Ind. Eng. Chem. Process Des. Dev.*, **22**, 582 (1983).

Manuscript received by AIChE Manuscript Center Mar. 4, 1986, received by AIChE Journal editorial office Dec. 8, 1986, and revision received Apr. 30, 1987.