

Chapter 3

Theory

3.1 Supercritical fluid [2]

The temperature at which the vapor pressure above the pure liquid reaches one atmosphere is known as the normal boiling point. For water, the normal boiling point at one atmosphere is 100 °C. In an open container, Figure 7, the temperature of liquid water can not be raised above 100 °C since this would cause the vapor pressure of water to rise above one atmosphere, which would exceed the ambient pressure conditions. If we place a quantity of liquid water in a sealed container, Figure 8, however, then we may heat to higher temperatures, since the vapor pressure of the water can now exceed one atmosphere. As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases. We can continue this heating process until the density of the liquid has been so reduced, and the density of the vapor phase has been so increased, that the two densities become equal. The temperature where the liquid and vapor densities become equal is called the critical temperature. Since the temperature inside the sealed container is everywhere equal, and the density is everywhere equal, thermodynamics dictates that the pressure inside the container be everywhere equal. This pressure is called the critical pressure. A fluid that has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid. The phase change from liquid and gas phases to supercritical phase is shown as Figure 9.

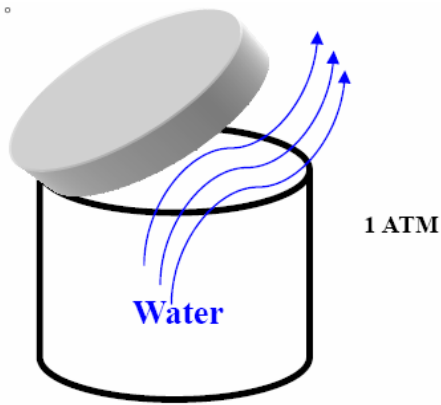


Figure 7 Opened container

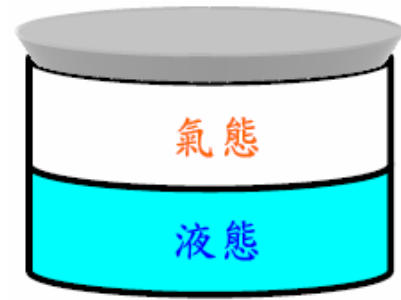


Figure 8 Sealed container

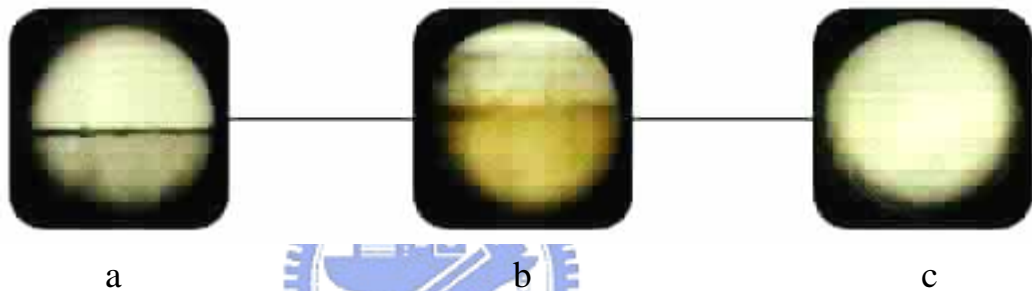


Figure 9 Cell (a) is at the lowest temperature and shows the liquid and gas phases with a meniscus between them. As the temperature and pressure rise and the density difference between the two phases becomes less, the meniscus becomes less distinct, as shown in cell (b). In practice the meniscus is no longer flat, because of temperature fluctuations and the small density difference. When the critical point is passed the meniscus disappears altogether, as shown in cell (c). Photographs of a real experiment of this type are shown below, in which the effects described can be seen in spite of the thermal turbulence present. [7]

3.2 Supercritical carbon dioxide

The physical description of the formation of a supercritical fluid suggests that all simple fluids can be made supercritical by generating the appropriate condition of temperature and pressure. This is indeed correct, and the Table 2 gives the critical

temperatures and pressures of some common fluids.

Table 2 Critical temperature and pressure for some common fluids [1]

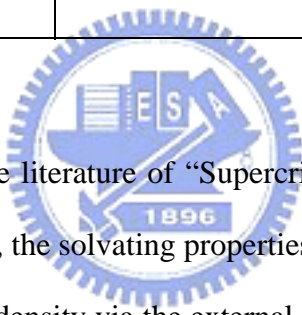
Fluid	Molecular formula	Critical pressure (PSI)	Critical temperature ()	Critical density (g/cm³)
Carbon dioxide	CO ₂	1072	31.1	0.443
Water	H ₂ O	3208.2	374.4	0.332
Ammonia	NH ₃	1646.2	132.4	0.235
Methane	CH ₄	667.2	-82.4	-
Ethane	C ₂ H ₆	697.6	32.2	0.203
Propane	C ₃ H ₈	616.4	96.8	0.217
Butane	C ₄ H ₁₀	543.9	135	0.228
Pentane	C ₅ H ₁₂	543.9	196.6	0.232
Ethane	C ₂ H ₆	720.8	9.2	0.218
Nitric oxide	N ₂ O	1039.9	36.5	0.450
Methanol	CH ₃ OH	1173.4	240.1	-
Isopropnaol	CH ₃ CHOHCH ₃	690.4	235.8	-

Carbon dioxide with appropriate critical pressure (31) and critical temperature (1072 psi). Carbon dioxide at its critical point, and in the supercritical fluid region of most interest. It is the high density of supercritical carbon dioxide, equaling the density of many liquid organic solvent, that contribute to the surprising solvent power of a supercritical fluid. At the same time as exhibiting a liquid-like density, supercritical carbon dioxide has diffusivity on the order of 100 X greater than a liquid, allowing for rapid transport properties. Simultaneously, the viscosity of a

supercritical carbon dioxide is closer to that of a gas, allowing for advantages in transport properties. The Table 3 [3] give the physical-chemical properties for carbon dioxide.

Table 3 physical-chemical properties for CO₂ [3]

	Liquid	Vapor	Critical Point	Supercritical Fluid
Density (g/cm ³)	1.0	$\sim 10^{-3}$	0.5	0.3 ~ 0.7
Diffusivity (cm ² /s)	$< 10^{-5}$	$\sim 10^{-1}$	$\sim 10^{-3}$	$10^{-2} \sim 10^{-5}$
Viscosity (g/cm-s)	$\sim 10^{-2}$	$\sim 10^{-6}$	$\sim 10^{-2}$	$10^{-3} \sim 10^{-6}$



According to the literature of “Supercritical Fluid Process for Semiconductor Device Fabrication” [3], the solvating properties of supercritical carbon dioxide can be varied by changing the density via the external temperature and pressure, so that some solvent selectivity can be achieved. Supercritical carbon dioxide behaves as a non-polar organic solvent, similar to hexane, and is therefore good for dissolving other non-polar materials. Small amounts of polar co-solvents can be added to enhance the solubility of polar materials. In addition, the low surface tension (approximate to “0”) of supercritical carbon dioxide makes it attractive for cleaning high aspect ratio structures. After the cleaning step, no rinsing with water or drying is needed since supercritical carbon dioxide evaporates completely upon depressurization to atmosphere.

Additional benefits of using carbon dioxide come from the fact that it is

non-toxic, non-flammable, non-corrosive, environmentally friendly, readily available in high purity and in large quantities, can be recycled, inert chemical property and inexpensive. The Figure 10 [3] give the phase diagram for carbon dioxide.

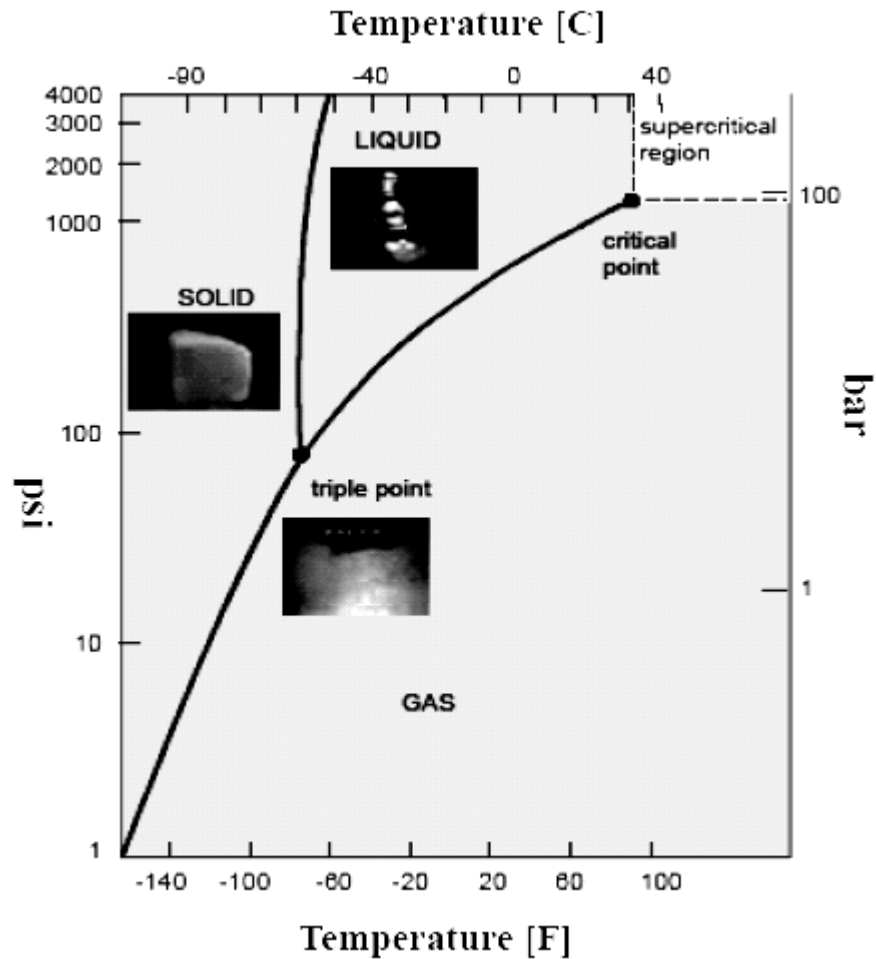


Figure 10 Phase diagram of CO₂ [3]

3.3 The mechanism of the photoresist removal using supercritical fluid

According to the literature of “ Supercritical Fluid Process for Semiconductor Device Fabrication ” [3], the photoresist is swollen by the diffusion of carbon dioxide into the matrix and that the co-solvent helps to degrade the polymer and break the bonds at the surface. After the photoresist is swollen and attack at the edges of the pattern has begun, continuing with the processing and introducing pulses of

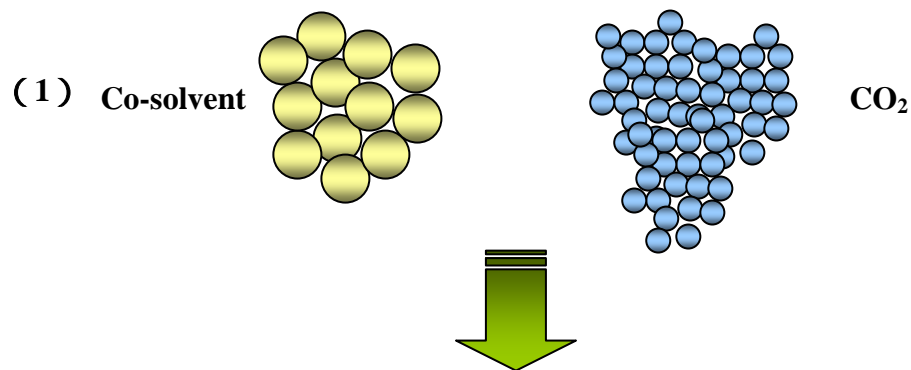
depressurization and repressurization (agitation step) show that the photoresist debonds from the surface and lift off in sheets. The additional requirement is that there be sufficient fluid flow to remove the debonded photoresist. If the fluid flow is insufficient, the debonded photoresist will remain on the surface.

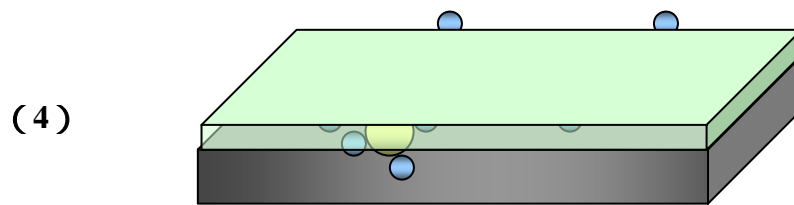
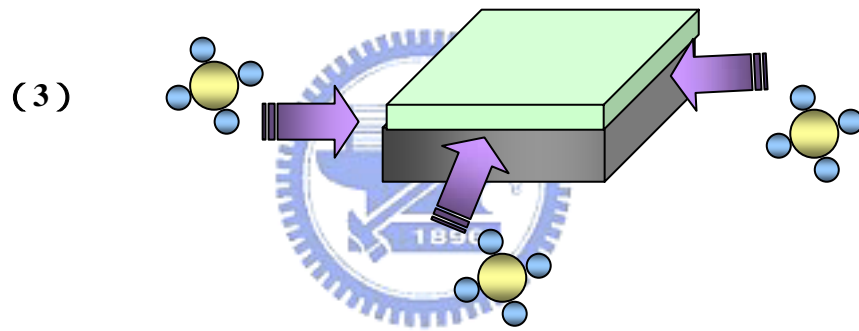
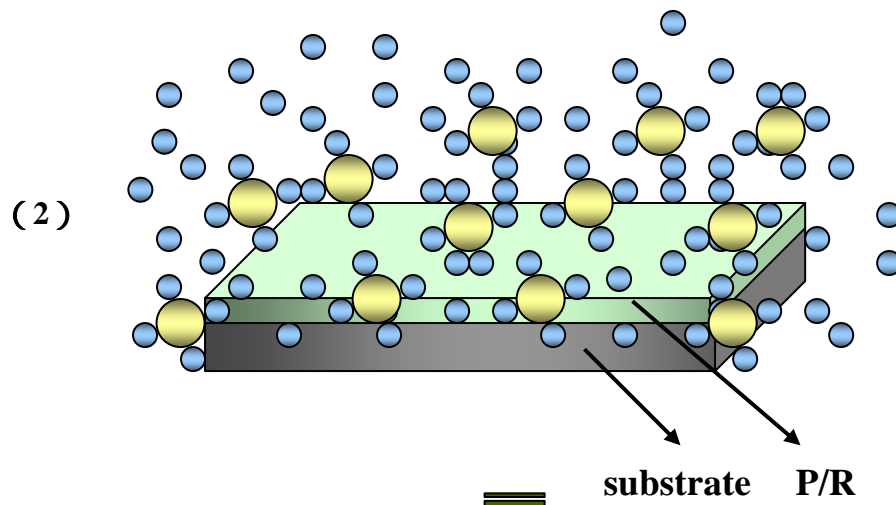
Two factors which affect a polymer ability to solubilize carbon dioxide are the crystallinity and the amount of crosslinking in the polymer. The presence of crystallinity in a polymer will inhibit the sorption of carbon dioxide. Highly cross-linked polymers will solubilize less carbon dioxide than those with less crosslinking. The sorption of carbon dioxide subsequently will result in swelling of the polymer, and is further enhanced if the glass transition temperature is exceeded. Additional disruption of polymer can occur through interactions with the solubilized carbon dioxide and/or co-solvent. Upon depressurization, the solubilized carbon dioxide begins to expand as the chamber pressure decreases. This expansion of the gas, and the reduced hydrostatic pressure exerted on the polymer, often results in a temporarily enhanced polymer swelling effect. Before the polymer/polymer interactions can be reestablished, stress crack, bubbles or complete debonding of the polymer film can occur as the carbon dioxide rapidly desorbs.

The process of removing photoresist and residue relies on the use of process materials such as carbon dioxide that tend to be good solvents especially at supercritical temperature and pressure, alone or in combination with useful additives such as co-solvent and surfactants selected to shift the critical point or improve the cleaning effect. The process materials are applied to the substrate preferably exclusively in gaseous and supercritical phase so as to avoid the problems associated with liquid contact.

The steps of soak and agitation are important especially in this process. Soak and agitation steps are applied to aid both chemically and mechanically in the removal of the unwanted material (photoresist and residues) from the substrate. The soak step permits infusion of the process materials into the unwanted materials at an elevated supercritical pressure. The agitation step includes a rapid decompression of the chamber after the soak period, still within supercritical pressure, in order to mechanically weaken and break loose pieces of the photoresist, sidewall polymer and such other materials as are sought to be removed, with a very significant pressure differential.

This is combined with a supercritical fluid flush to carry away the loose debris, and is then preferably concluded by rapidly elevating the chamber pressure back to the higher supercritical pressure, stressing the unwanted materials this time with rapid compression. The diagram of the mechanism of photoresist removal is shown as the Figure 11.





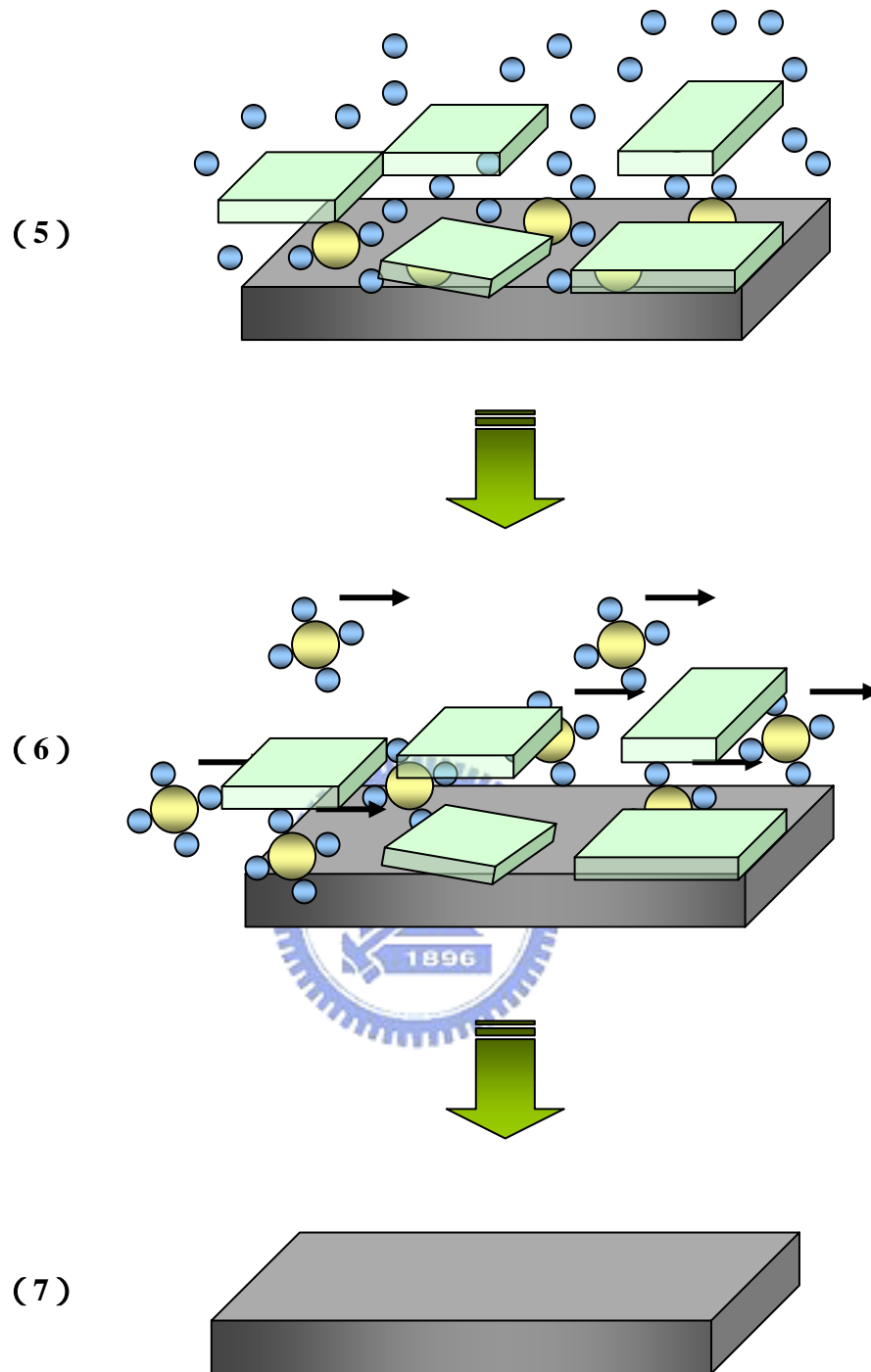


Figure 11 The mechanism of P/R removal

- (1) Carbon dioxide and co-solvent infused into the chamber together.
- (2) Co-solvent is solved in supercritical carbon dioxide and fulfilled the chamber at high pressure, the sample immersed in the mixture of

supercritical carbon dioxide and co-solvent.

- (3) The role of carbon dioxide molecule is a carrier material, and carried the co-solvent molecule into the interface between photoresist and substrate from the edges of sample; The role of co-solvent molecule helps to degrade the polymer and break the bonds at the surface.
- (4) Carbon dioxide and co-solvent have infused into the interface between photoresist and substrate.
- (5) The chamber rapid decompression, and then the carbon dioxide began to expand, the photoresist is swollen and debonded from the surface and lift off in sheets. A portion of co-solvent is still state on the surface on the substrate, and the others are carried away by carbon dioxide from the substrate.
- (6) The sufficient fluid flow to remove the debonded photoresist and residues.
- (7) The sample has been cleared.

Because the photoresist with a hard crust on top (due to the implantation or etching process, the photoresist resulted in more cross-link on top.) , and the co-solvent can not infuse into and dissolve the hard crust. Therefore, the co-solvent degrade the photoresist and break the bonds from the edges. (Figure 12) .

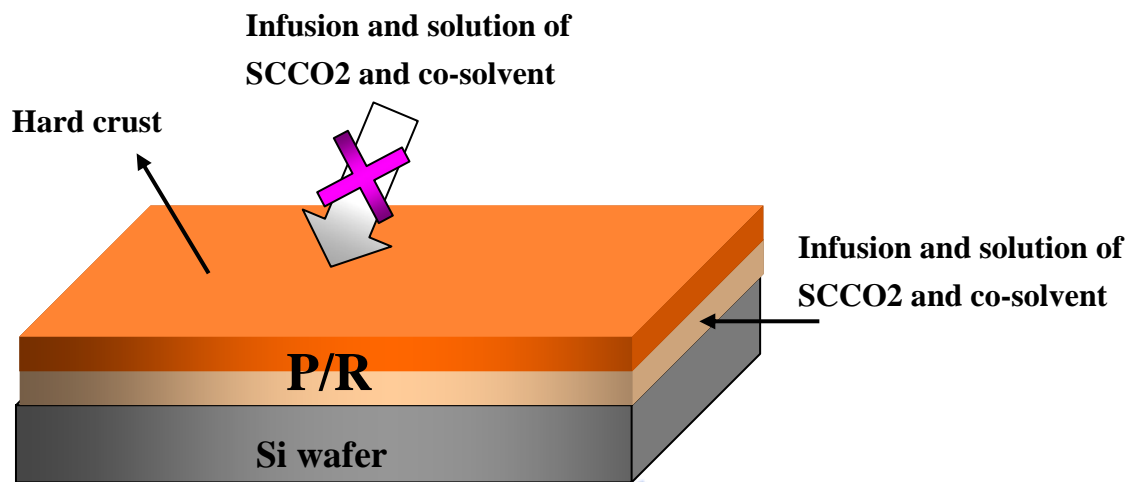


Figure 12 The hard crust of photoresist after the ion implantation or etching process, and indicating the direction of diffusion and solution of SCCO₂ and co-solvent