

# Chapter1

## Introduction

### 1.1 General Background

The growth of the integrated circuits (IC) is primarily based on increasing circuit performance and the functional complexity of the circuits. To achieve the goal, scaling down of active device sizes and increasing interconnect packing density are very effective means. But scaling the device, the line width and space between metal interconnections also become small. This process will increase the RC time delay, which is due to the higher wire resistance (R) of narrower metal lines and the higher intra/inter- level capacitance (C) between the tightly spaced interconnections. As a result, the characteristics of the interconnections will be an important factor of RC time delay.[1-2].

The delay effect is shown in Fig1-1, we assume that the minimum metal pitch equals twice the metal width and the dielectric thickness. This assumption is the same as that of the metal lines in between Fig 1-2. With the first-order approximation, time delay  $\tau$  and power consumption P can be obtained respectively as following:

$$R = \rho \frac{L_m}{W t_m}$$

$$C = 2(C_L + C_v) = 2\varepsilon \left[ \frac{L_m t_m}{W} + \frac{L_m W}{t_m} \right]$$

$$\tau = RC = 2\rho\varepsilon \left[ \frac{L_m^2}{W^2} + \frac{L_m^2}{t_m^2} \right]$$

$$P \propto 2\pi f V^2 \varepsilon \tan(\delta)$$

$$\therefore P \propto 2\pi f V^2 C$$

Where  $\rho$  is the resistivity,  $L_m$  is the interconnect line length,  $W$  is the interconnect line width,  $\varepsilon$  is the permittivity,  $t_m$  is the thickness of the metal, and  $f$ ,  $V$  and  $\tan(\delta)$  are frequency, applied voltage and dielectric loss. Based on these equations, reducing RC time delay can be divided to resistance or the capacitance. Copper has a resistivity ( $1.7 \mu\Omega\text{-cm}$ ) much lower than the Al-Cu material ( $2.7\mu\Omega\text{-cm}$ ). So using copper wiring instead of Al interconnection for multi interconnects is the solution to reduce the metal line resistance.[3-4] On the other hand, a low dielectric constant material ( $k < 3.0$ ) is needed to reduce the coupling capacitance between the metal lines for reduction of signal propagation delay, and it also reduces cross-talk noise in interconnections and alleviates power dissipation issues. [5]

## 1.2 Introduction to Supercritical Fluid Processes

Supercritical fluids are compounds above their critical temperatures and pressure.

( Fig 1-3) [6-7] Table1 shows critical temperature and pressure for some common

fluids. And they are used in many commercial applications, including the extraction of caffeine from coffee, fats from foods, and essential oils from plants for use in perfumes. CO<sub>2</sub>-based supercritical fluids are particularly attractive because CO<sub>2</sub> is non-toxic, non-flammable, and inexpensive. Its critical conditions are easily achievable with existing process equipment (31 °C , 1072 psi =72.8atm).

The attractiveness of supercritical fluids for commercial applications are their unique combination of liquid-like and gas-like properties. Table2 shows the comparison of several physical properties of typical liquid, vapor, and supercritical fluid state. It can be seen that high density of supercritical fluids, possessing a liquid-like density. This gives the fluid the ability, much like that of a light hydrocarbon (i.e. pentane), to dissolve most solutes [8]. Also supercritical fluids are gas-like in respect to their very low viscosity and little to no surface tension allowing them to enter the smallest pores or spaces on a wafer. These properties are what make supercritical fluids so appealing for cleaning, extraction, and chromatography.[9]

Figure 1-4 shows the density- pressure-temperature surface for pure CO<sub>2</sub>. It can be seen that relatively small changes in temperature or pressure near the critical point, result in large changes in density. These properties are what make supercritical fluid technology so attractive for the cleaning process.

### 1.3 Motivation

In multilevel manufacturing, up to 20% of all process steps are cleaning wafer surface, consuming of large quantities of chemicals and pure water.[10] And photoresist stripping is one of the process consuming large amounts of chemicals and water.

Today photoresist removal is commonly performed with dry stripping process and wet stripper solution. Dry stripping process includes both the O<sub>2</sub> plasma step for removing most of photoresist and a wet stripping process for removing the residues.

[11] Besides, low dielectric constant material damaged by O<sub>2</sub> plasma process easily deteriorates organosilicate glass, causing a significant increase of leakage current and dielectric constant.[12-14]



Wet stripping processes are corrosive and toxic materials, which are difficult to handle and dispose.[15] And the accumulated contaminates reduce the stripping effectiveness in the bath. Also the wet stripper often leads to the hydrolysis of low dielectric constant material. It will tend to uptake water and consequently increase both leakage current and dielectric constant.[16]

Both of these processes have hazardous chemicals to the environment and damage to the low dielectric constant materials, so supercritical fluid can be noticed for its excellent ability for stripping photoresist.

The purpose of this study will discuss the photoresist stripping by supercritical CO<sub>2</sub> with co-solvents, and the influence of supercritical CO<sub>2</sub> integrated to the backend process.



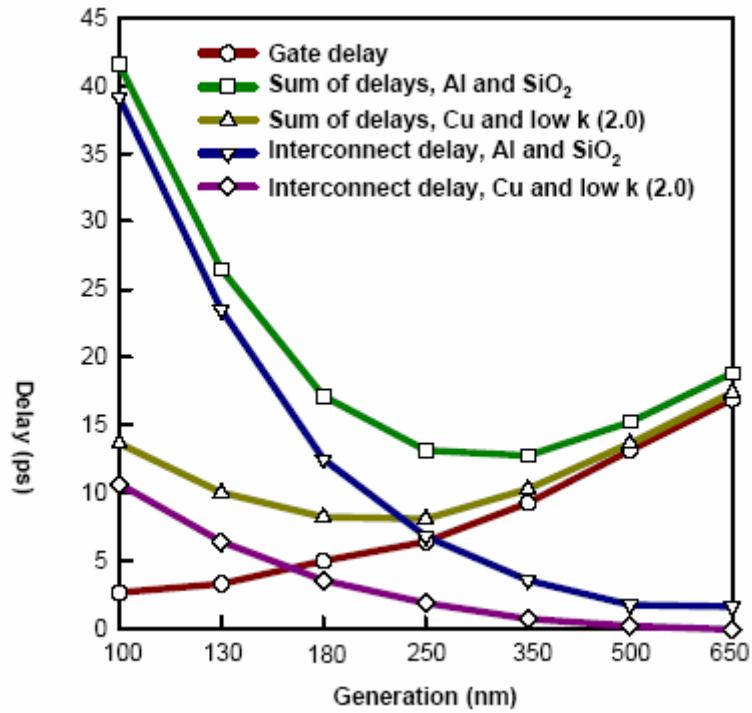


Fig 1-1 Decrease in interconnect delay and improved performance are achieved using copper and low-k dielectric. (Source: ITRS)

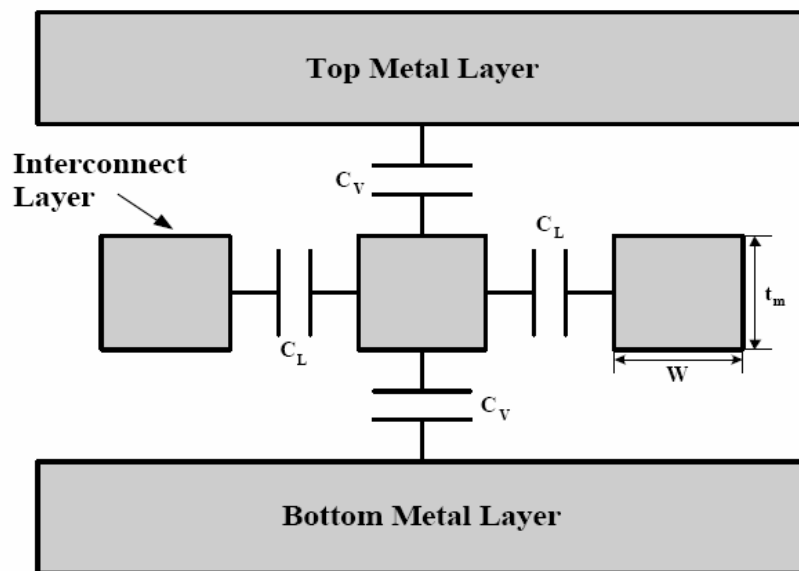


Fig 1-2 The cross-section of interconnect system with parasitic capacitance.

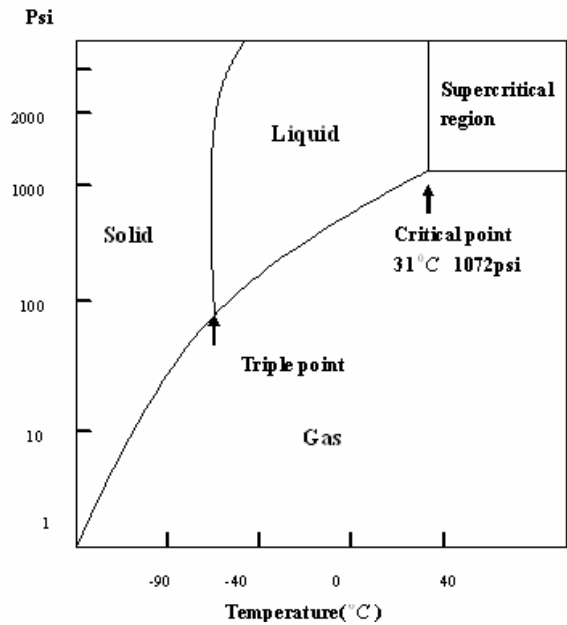


Fig 1-3 Phase diagram for CO<sub>2</sub>

Fluid	Critical Temperature(°C)	Critical Pressure (Psi) (1atm=14.7psi)
Helium (He)	-268	33
Neon (Ne)	-229	400
Argon (Ar)	-122	706
Nitrogen (N <sub>2</sub> )	-147	492
Oxygen (O <sub>2</sub> )	-119	731
Carbon dioxide (CO <sub>2</sub> )	31	1072
Sulfur hexafluoride (SF <sub>6</sub> )	46	545
Ammonia (NH <sub>3</sub> )	133	1654
Water (H <sub>2</sub> O)	374	3209

Table 1 Critical temperature and pressure for some common fluids

	Liquid	Supercritical fluid	Vapor
Density( $\text{g/cm}^3$ )	1.0	0.3-0.7	$\sim 10^{-3}$
Diffusivity( $\text{cm}^2/\text{sec}$ )	$< 10^{-5}$	$10^{-2} - 10^{-5}$	$\sim 10^{-1}$
Viscosity( $\text{g/cm-sec}$ )	$\sim 10^{-2}$	$10^{-3} - 10^{-6}$	$\sim 10^{-6}$

Table 2 Comparison of physical properties of  $\text{CO}_2$

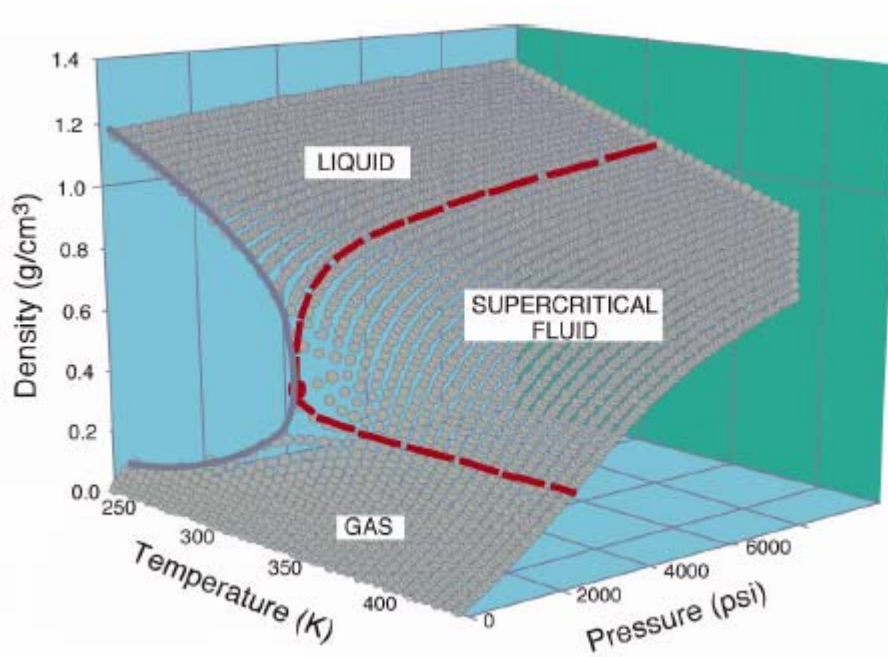


Fig1-4 Density- pressure-temperature surface for pure  $\text{CO}_2$

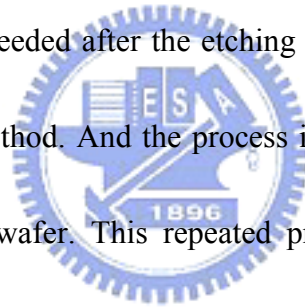


# Chapter 2

## Effects of Photoresist Stripping by Supercritical CO<sub>2</sub>

### 2.1 Current Photoresist Stripping Processes

As semiconductor device manufacturing and IC fabrication continue to shrink, it requires precisely controlled patterns on the silicon substrate. Lithographic processes create the patterns required. After a series of steps, such as development and etching, the photoresist is no longer needed after the etching process. It must be removed by solvents or by dry plasma method. And the process is repeated and could take place up to thirty times for each wafer. This repeated process adds to the concern for reducing the cost and increasing the effectiveness of the process.

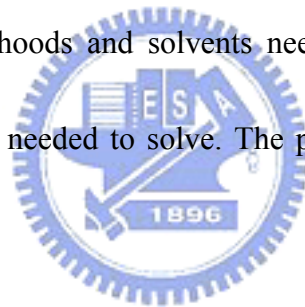


There are two main processes of photoresist stripping. One process is wet stripping utilizing solvents, and the other is called dry stripping and uses plasma.

Wet stripping is the favored process because of its history, cost effectiveness, and removal of metal ions. But semiconductor device dimensions approach the nanoscale, it will become increasingly difficult to use aqueous-based wetting processes due to high surface tension and capillary forces. And the solvents used for wet stripping can be grouped into acids and organic solvents. The solvents are very

corrosive and are irritants to mucous membranes and skin as well as a possible carcinogen. This acid emits highly toxic vapors when heated. Besides, the wet stripper may cause the hydrolysis of low dielectric constant material, and increases the leakage current and dielectric constant.

The other photoresist stripping process is dry stripping method. During plasma process, photoresist is removed by oxygen energized in a plasma field, which oxidizes the resist components to gases that are removed from the process chamber by a vacuum pump. The main advantage of utilizing a dry stripping process is the elimination of the chemical hoods and solvents needed for wet stripping. But the plasma process has problems needed to solve. The problems can be summarized as follows:



After plasma process, residues are left in vias and trenches that need additional wet chemical treatment;

Plasma process is performed at high temperatures, adding to the thermal budget of the wafer;

Plasma process is not efficient for removing mobile metallic ion contamination;

Plasma process can cause radiation damage of the electronic circuits;

With Plasma process, selectivity between photoresist and low k materials is bad and low-k material may be mechanically affected;

Plasma process can modify the dielectric constant of low k material due to charge damage;

Post-strip wet chemical treatment may modify the low k material in its electrical properties;

Shrinking dimensions of features below 0.18  $\mu\text{m}$  present a problem for wet chemistry as post-strip cleans method, because of surface tension issues.

Although current photoresist stripping processes are effective at removing most photoresist, it was found that wetting processes are limited in the reduction of microchip size due to their physical properties. Also, the solvents have a short lifetime. This requires disposing and replacing the solvents frequently.

The purpose of this study was to analysis the supercritical carbon dioxide for use in the photoresist removal process to overcome current process barriers.

## **2.2 Mechanism of Striping Photoresist by Supercritical Carbon Dioxide**

Supercritical fluids are compounds above their critical temperature and pressure. The critical point for pure  $\text{CO}_2$  occurs at temperature of  $31^\circ\text{C}$ , and pressure 1072 psi (72.8 atm). The relatively small changes of temperature and pressure, above the critical point, will result in large changes of  $\text{CO}_2$  density. The tenability of density is

one of the most attractive attributes of supercritical fluids. The gas-like properties of low viscosity and high diffusivity are allowed for rapid transport into micro-porous matrices. And the liquid-like property of density provides for transport and dissolving properties.[17]

The use of supercritical carbon dioxide as a photoresist stripper has been researched. [18-20] Rubin[18] observed that supercritical carbon dioxide behaves as a non-polar organic solvent, similar to hexane, and is good for dissolving other non-polar materials.[21] Small amounts of polar cosolvents can be added to enhance the solubility of polar materials.[22-24] And supercritical carbon dioxide can clean high aspect ratio structures by low surface tension character. In addition, Rubin developed a closed-loop system for supercritical carbon dioxide and cosolvents. The system was effective in stripping photoresist and no rinsing or drying is needed in other instrument.

The mechanism for stripping photoresist by supercritical carbon dioxide has not clearly determined. However, it is well known that the mechanism for photoresist baked or implanted and RIE etched is different. The baked photoresist is easily stripped by supercritical carbon dioxide with co-solvent. But the photoresist implanted or exposed to reactive ion etching will be difficult tripped.

Rubin speculate that the photoresist is swelled by the diffusion of carbon dioxide

into the matrix. It will effectively soften the photoresist. The co-solvent degrades the polymer and breaks the bonds at the surface. And repeated depressurization and repressurization promotes the photoresist stripping. Finally fluid flows carry away the debonded photoresist.

Recently, the other article [25] has shown a method for the photoresist removal process by supercritical carbon dioxide. Soak and agitation steps are applied to the wafer, including a rapid decompression of the process chamber after a soak period at higher supercritical pressure, to mechanically weaken and break loose pieces of the photoresist, sidewall polymer and such other materials as are sought to be removed, with a significant pressure differential.



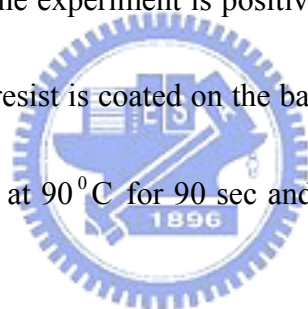
The soak step at an elevated supercritical pressure permits infusion of supercritical carbon dioxide and solvents into the unwanted matter. The agitation step follows the soak step. The agitation step includes a rapid decompression of the process chamber in supercritical pressure, in order to mechanically weaken and break loose pieces of the photoresist, sidewall polymer and such other materials are sought to be removed, with a very significant different pressure. Combined with a supercritical fluid flush to carry away the loose debris, and is then preferably concluded by rapidly elevating the vessel pressure back to the higher supercritical pressure, stressing the unwanted material times with rapid compression. The core

process steps are preceded and followed by more conventional loading and unloading steps, except that the purging and pressurization steps avoid any liquid contact with the substrate, constraining the inflowing process materials to process gas and supercritical fluid.

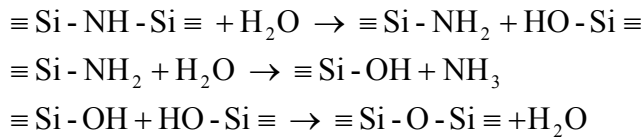
## 2.3 Experimental procedures

The purpose of the experiment is to verify the photoresist stripping by supercritical carbon dioxide with co-solvent.

The photoresist used in the experiment is positive photoresist, and is compatible for I-Line process. The photoresist is coated on the bare silicon and low-K MSZ film. Then the photoresist is baked at 90<sup>0</sup>C for 90 sec and 110<sup>0</sup>C for 60 sec for soft and hard bake.



The MSZ film is formed as follows. The wafer was spun coated with a methyl-silsesquioxane (MSZ) solution. The spin speed is about 2000 rpm for 30 sec. Then the wafer is baked at 150<sup>0</sup>C and 280<sup>0</sup>C for 3minutes. Then the wafer was in clean room for 48 hours in order to carry out hydration. The precursor-structure of MSZ film will be transformed to methyl-silsesquioxane through hydrolysis and condensation process, shown as follows:



Afterward, the coated wafer was cured in quartz furnace at 400<sup>0</sup>C for 30 min under N<sub>2</sub> ambient. The final MSZ film was formed to about 230nm. The structure properties of MSZ film was studied using Fourier-transform infrared spectroscopy (FTIR) in Fig 2-1.

The co-solvents used in the experiment are PCO<sub>3</sub> [25-26] and propyl alcohol. Propylene carbonate, abbreviated PCO<sub>3</sub> shown in Fig 2-2 is effective to remove hard-baked photoresist. PCO<sub>3</sub> is an environmentally-friendly solvent and is non-flammable, non-toxic, biodegradable, and has a low vapor pressure. Besides, PCO<sub>3</sub> is completely miscible with high pressure carbon dioxide.

For the experiment, Fig 2-3 shows the schematic drawing of the supercritical carbon dioxide treatment system. Pump A feeds a high-pressure syringe pump, supplies high-pressure ambient-temperature CO<sub>2</sub>. Pump B feeds a high-pressure syringe pump, supplies solvents. The sample is setting in the pressure chamber. And the flow rate is restricted by modulated tube.

The photoresist is coated on the bare silicon and low-K MSZ film. Then the wafer is cut into pieces suitable for the size of pressure chamber. The experiment flow is illustrated as a block diagram in Fig 2-4. The temperature of chamber is set for

50<sup>0</sup> C, and PCO<sub>3</sub> and propyl alcohol are used for co-solvent. Also, we change the percent of co-solvent as 1%, 5%, 9%. The experiment begins by placing the sample within the pressure chamber in a first process step.

In a second process step, the syringe pumps of Pump A and Pump B (Fig2-3) are pressurized to 1100 psi, and then the supercritical CO<sub>2</sub> carries the co-solvent into pressure chamber. The step provides for that CO<sub>2</sub> and co-solvent in supercritical fluid state. In a third process step, the syringe pumps of Pump A and Pump B are pressurized to 1600 psi, and more co-solvents are carried by supercritical CO<sub>2</sub> into the chamber. During this soak step, the supercritical CO<sub>2</sub> and co-solvent are maintained in contact with the wafer, and the co-solvent partially dissolve the photoresist.

In a fourth process step, the syringe pumps of Pump A and Pump B are de-pressurized to 1100 psi, and provide supercritical CO<sub>2</sub> and co-solvent to flush through the chamber. During this flush step, co-solvent also partially dissolves the photoresist, and supercritical CO<sub>2</sub> carry away the dissolved photoresist.

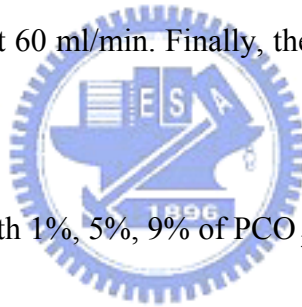
From a second step to a fourth step, it is called” **process step**”, and the photoresist is not removed completely. The process step is performed for 1, 2, 3 cycles.

After photoresist removed completely, it is followed by dry step. In a fifth process step, the sample is soaked by supercritical CO<sub>2</sub> at 3000psi. Then it is flushed



by supercritical CO<sub>2</sub> at 3000psi in a sixth process step. The dry step is performed to carry away the solvent on the wafer. And three cycles of dry step is needed to dry the sample. Finally, in a seventh process step, the experiment ends by depressurizing the pressure chamber and removing the wafer.

The experiment flow is illustrated as a diagram in Fig 2-5. The time of first step is from 0 to t<sub>0</sub>. The time of second step from t<sub>0</sub> to t<sub>1</sub> is 1 min, and the time of fifth step from t<sub>6</sub> to t<sub>7</sub> is 1 min. The flush time of the fourth step from t<sub>4</sub> to t<sub>5</sub> is 2 min, and the flow rate is about 20 ml/min. And the flush time of the sixth step from t<sub>7</sub> to t<sub>8</sub> is 1 min, and the flow rate is about 60 ml/min. Finally, the time of seventh process step is from t<sub>8</sub> to t<sub>9</sub>.



We perform the samples with 1%, 5%, 9% of PCO<sub>3</sub> and propyl alcohol, and change the process step for 1, 2, 3, cycles. By the way, **excluding** the time from 0 to t<sub>0</sub> for the first process step, and the pressurized time from t<sub>1</sub> to t<sub>2</sub>, and from time t<sub>5</sub> to t<sub>6</sub>, and the seventh process step from t<sub>8</sub> to t<sub>9</sub>, the total experiment time for 1 cycle of process step and 3cycles of dry step is 10 min. And the experiment time for 2 cycles of process step and 3cycles of dry step is 14 min. And the experiment time for 3 cycles of process step and 3cycles of dry step is 18 min.

Fig 2-6 shows that photoresist coated on the bare silicon are stripped by supercritical CO<sub>2</sub> and PCO<sub>3</sub> with different percent of co-solvent and cycles of process

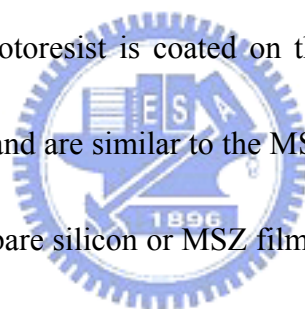
step. We took the photos by microscope. While the effects for the photoresist on the bare silicon stripped by supercritical CO<sub>2</sub> with PCO<sub>3</sub>, and the photoresist on the MSZ film stripped by supercritical CO<sub>2</sub> with PCO<sub>3</sub> or propyl alcohol are similar, so we show Fig 2-6 for example. And Fig 2-7 represents the FTIR spectra for the photoresist coated on the bare silicon and low-K MSZ film stripped by that 3 cycles of process step and 3cycles of dry step with 5 % PCO<sub>3</sub> or 5% propyl alcohol.

## 2.4 Result and discussion

The photoresist on the bare silicon stripped by supercritical CO<sub>2</sub> with PCO<sub>3</sub> is exhibited, and the pictures are shown in Fig 2-6. In Fig 2-6, the effects of 1, 2, 3 cycles of process step and 1, 5, 9 % of PCO<sub>3</sub> are compared. We find that the hard-baked photoresist is dissolved by PCO<sub>3</sub>, and the more cycles of process step or more percent of PCO<sub>3</sub> will improve the photoresist stripping. It shows that 5% of PCO<sub>3</sub> and 3 cycles of process step is needed to strip photoresist. The effect for propyl alcohol is similar to PCO<sub>3</sub>. And the photoresist coated on the MSZ film stripped by supercritical CO<sub>2</sub> with PCO<sub>3</sub> or propyl alcohol is confirmed in the experiment. In Fig.2-7, FTIR pictures show the effect for photoresist stripping. The photoresist is treated by 3 cycles of process step and 5% or 9% of PCO<sub>3</sub> or propyl alcohol. The intensities of H<sub>2</sub>O groups (~3400 cm<sup>-1</sup>) increase when photoresist is coated on the bare silicon. And the C-H peaks (~2974, ~1470cm<sup>-1</sup>) also increase. After the

photoresist is stripped by supercritical CO<sub>2</sub> with PCO<sub>3</sub> and propyl alcohol, the C-H peaks which are the main bond of the photoresist decrease significantly, and are similar to the peak of bare si. This means that photoresist is stripped completely. And we find that H<sub>2</sub>O groups increase when photoresist is coated. After the photoresist is stripped, the H<sub>2</sub>O groups decrease significantly. This means that the dry step of the stripping process is effective for removing moisture and solvent.

Fig.2-7-3 and Fig.2-7-4 show the FTIR pictures of the photoresist on the MSZ film stripped by supercritical CO<sub>2</sub> with PCO<sub>3</sub> and propyl alcohol. The H<sub>2</sub>O groups and C-H peaks increase when photoresist is coated on the MSZ film. After photoresist stripping, the peaks decrease and are similar to the MSZ film. So, we can confirm that the photoresist coated on the bare silicon or MSZ film can be stripped by supercritical CO<sub>2</sub> with PCO<sub>3</sub> or propyl alcohol.



## 2.5 Summary

The current photoresist stripping by solvents or by plasma is useful. But problems caused by stripping process can be summarized as follows: The hazards and toxicity of solvents are harmful to human and environment. It needed to continually purchase and replace the solvents since they have a short time of effectiveness, and it is costly. Besides, the surface tension of water will occur for small features. And photoresist stripping by solvents or by plasma will damage the low-K film in previous

work.

The supercritical carbon dioxide with solvents is another method to strip photoresist. It is not harmful to human and environment, and it needs less solvent in the process. Besides, the damage to film is minimal by supercritical CO<sub>2</sub>.

In the experiment, we find that hard-baked photoresist can be dissolved by solvents. More cycles of process step and solvent will strip more photoresist. And the FTIR pictures help us to confirm the effect. In next chapter, the process will be integrated to MSZ film. We will analyze the supercritical CO<sub>2</sub> impacts of MSZ film.



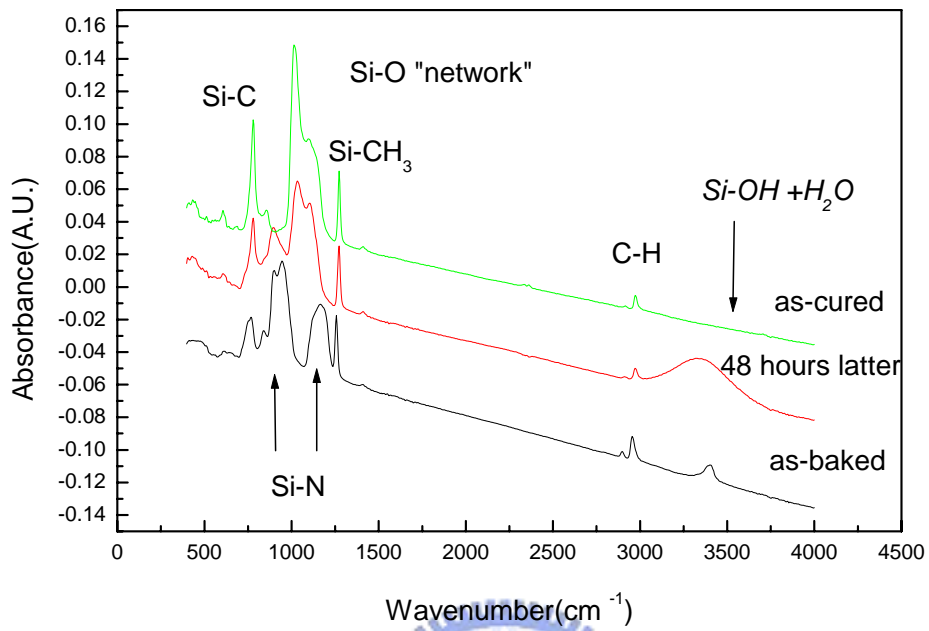


Fig 2-1 FTIR spectra of MSZ formation

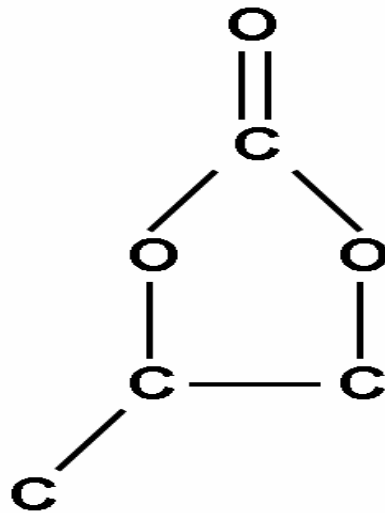


Fig 2-2 Structure of Propylene carbonate (PCO<sub>3</sub>)

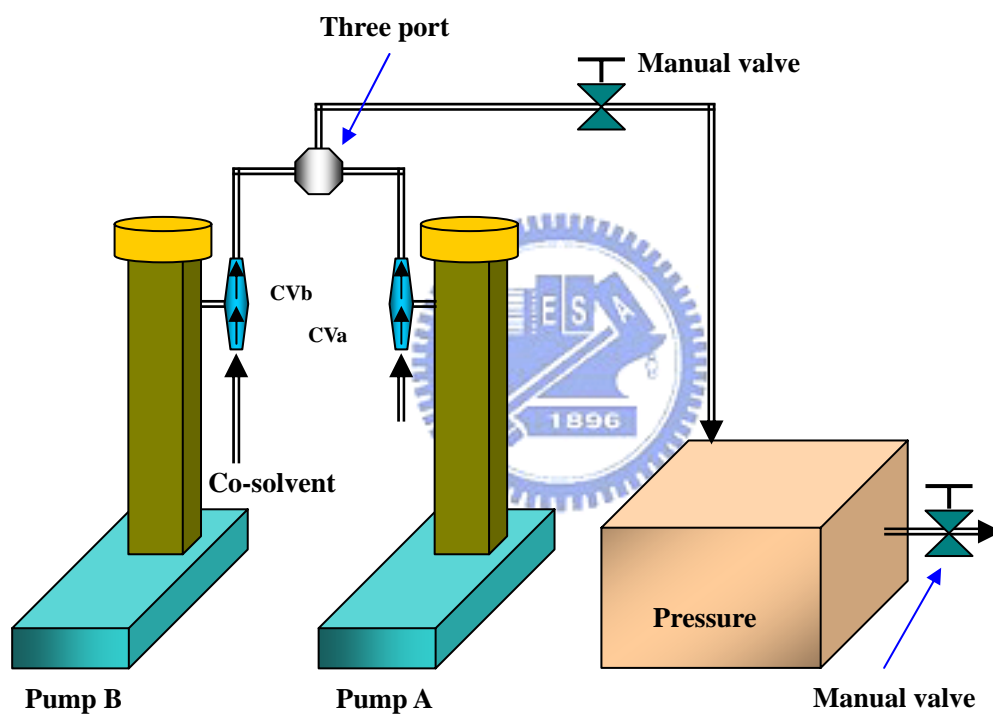
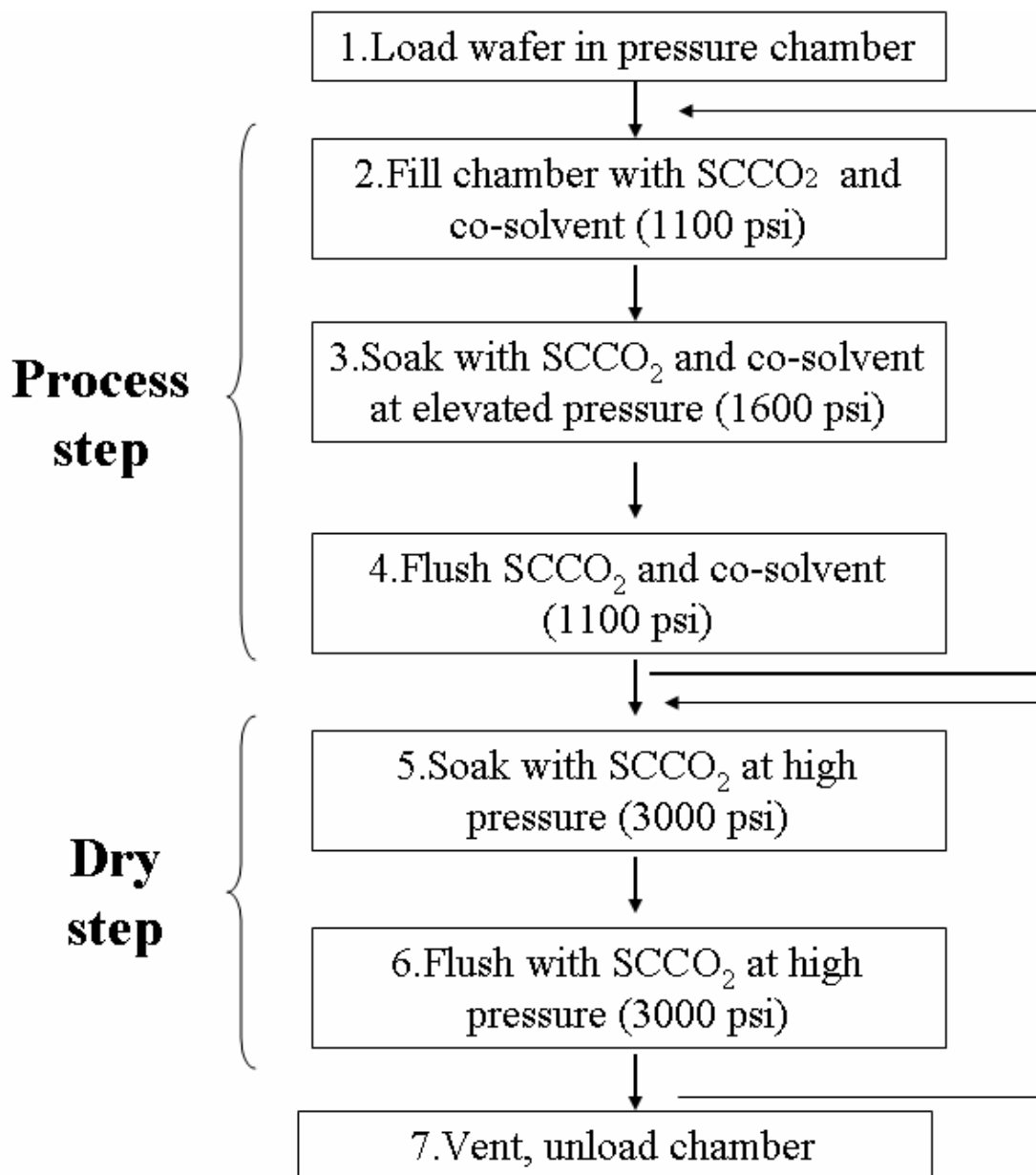


Fig 2-3 the schematic drawing of the supercritical carbon dioxide treatment system.



**Fig 2-4** The experiment flow

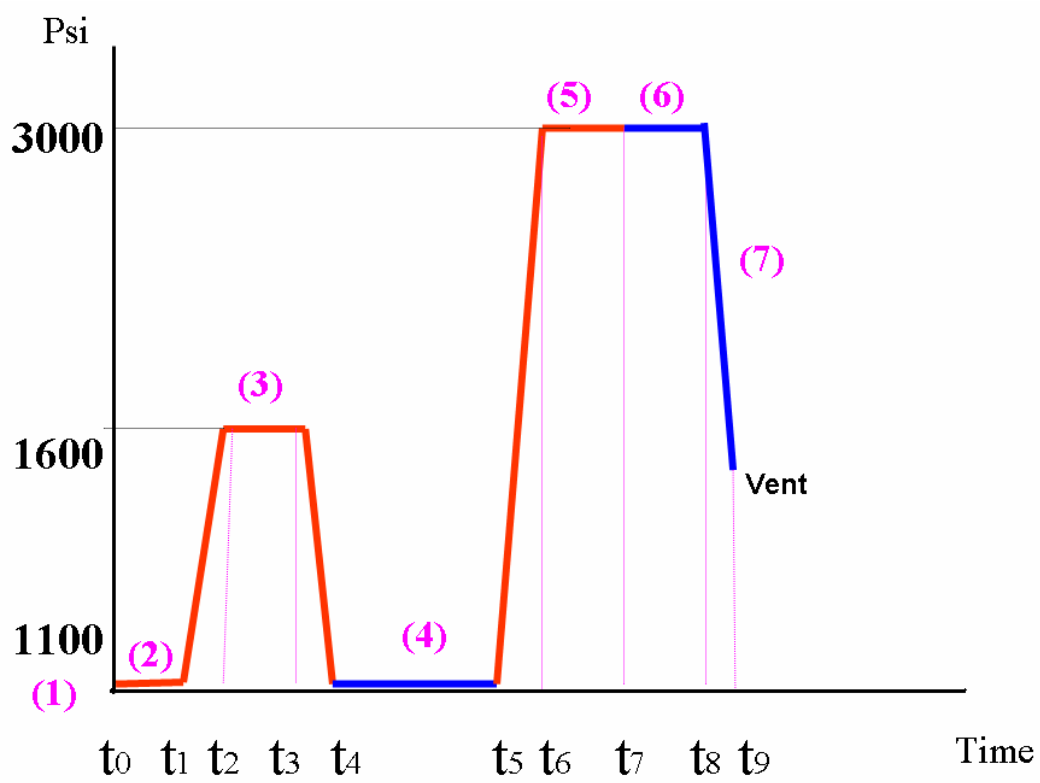


Fig 2-5 The timeline of the experiment





Fig 2-6-1 photoresist stripping by supercritical  $\text{CO}_2$  with 1 %  $\text{PCO}_3$ ,  
1 cycle of process step and 3 cycles of dry step

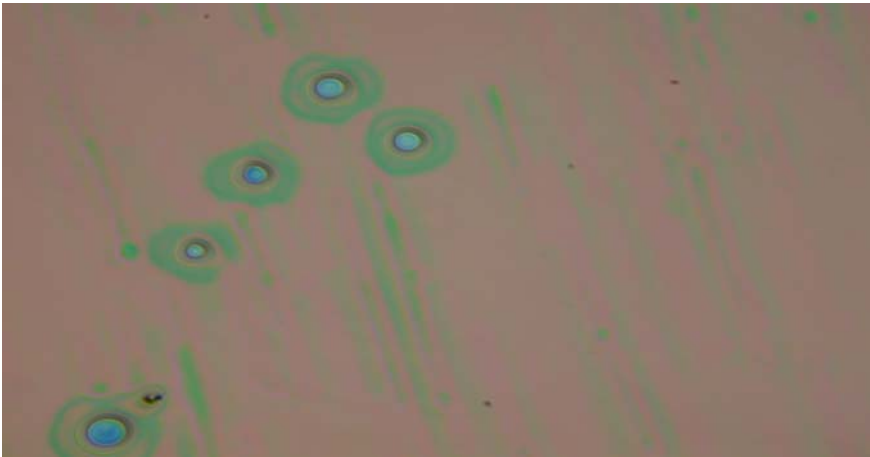


Fig 2-6-2 photoresist stripping by supercritical  $\text{CO}_2$  with 1 %  $\text{PCO}_3$ ,  
2 cycles of process step and 3 cycles of dry step

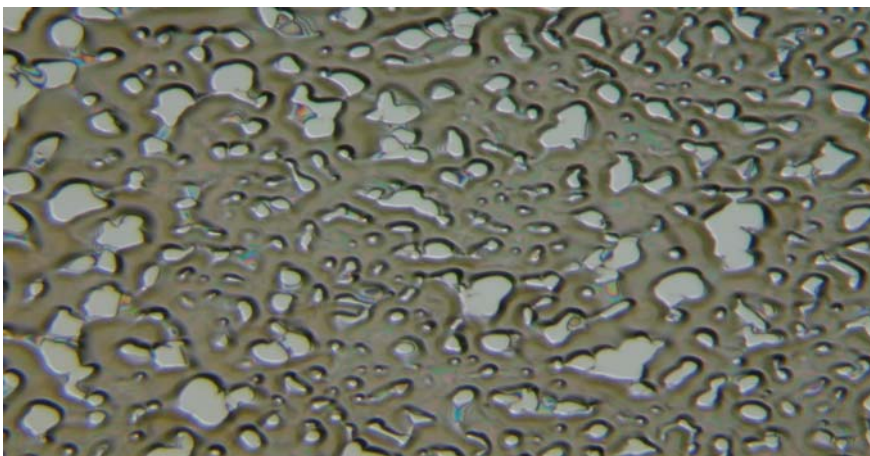


Fig 2-6-3 photoresist stripping by supercritical  $\text{CO}_2$  with 1 %  $\text{PCO}_3$ ,  
3 cycles of process step and 3 cycles of dry step

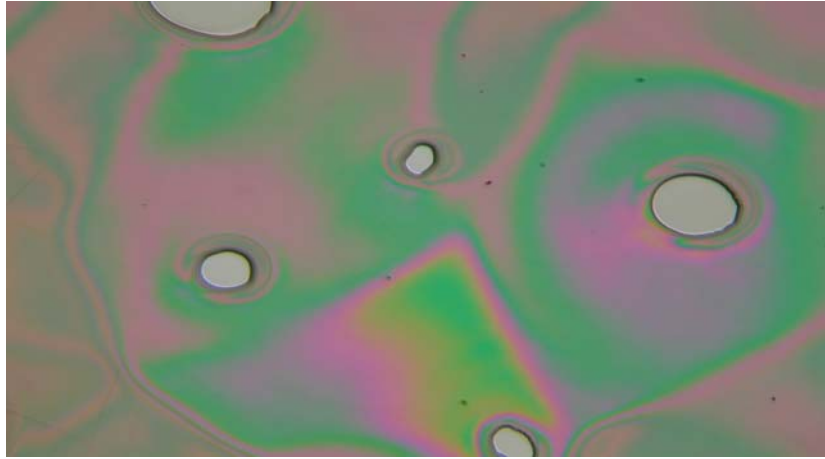


Fig 2-6-4 photoresist stripping by supercritical  $\text{CO}_2$  with 5 %  $\text{PCO}_3$ ,  
1 cycle of process step and 3 cycles of dry step

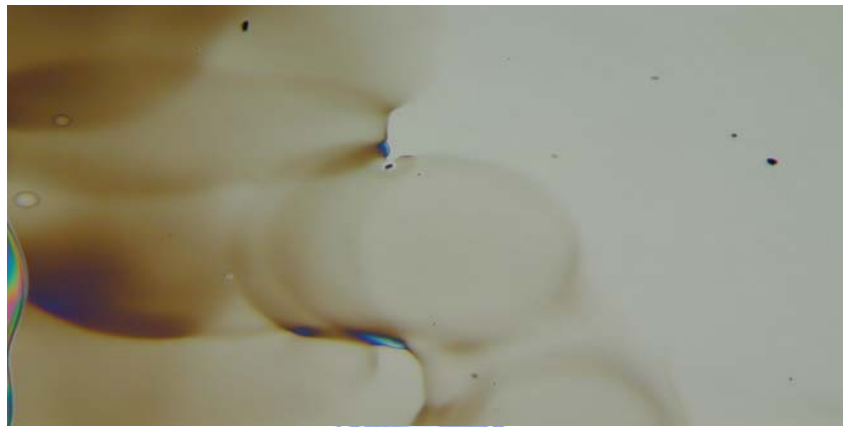


Fig 2-6-5 photoresist stripping by supercritical  $\text{CO}_2$  with 5 %  $\text{PCO}_3$ ,  
2 cycles of process step and 3 cycles of dry step



Fig 2-6-6 photoresist stripping by supercritical  $\text{CO}_2$  with 5 %  $\text{PCO}_3$ ,  
3 cycles of process step and 3 cycles of dry step

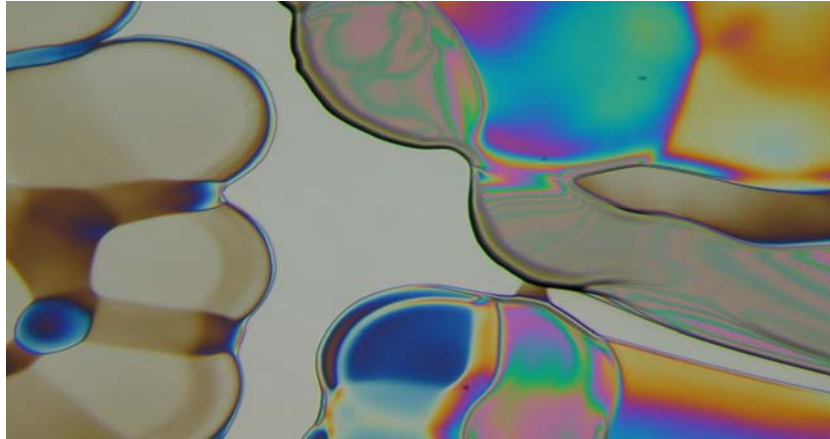


Fig 2-6-7 photoresist stripping by supercritical  $\text{CO}_2$  with 9 %  $\text{PCO}_3$ ,  
1 cycle of process step and 3 cycles of dry step



Fig 2-6-8 photoresist stripping by supercritical  $\text{CO}_2$  with 9 %  $\text{PCO}_3$ ,  
2 cycles of process step and 3 cycles of dry step



Fig 2-6-9 photoresist stripping by supercritical  $\text{CO}_2$  with 9 %  $\text{PCO}_3$ ,  
3cycles of process step and 3 cycles of dry step

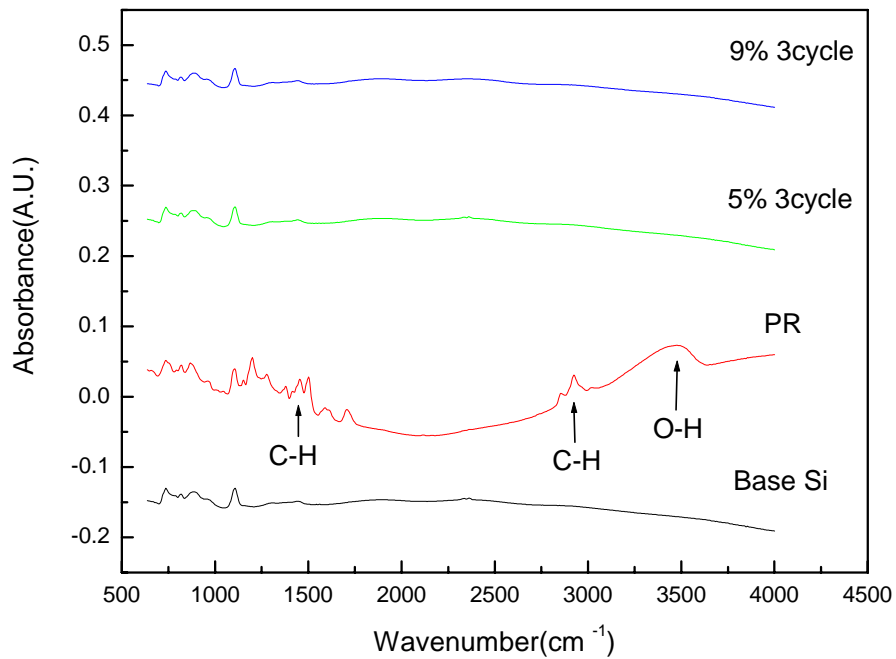


Fig 2-7-1 FTIR spectrum of photoresist stripping on bare silicon by supercritical CO<sub>2</sub> with PCO<sub>3</sub>

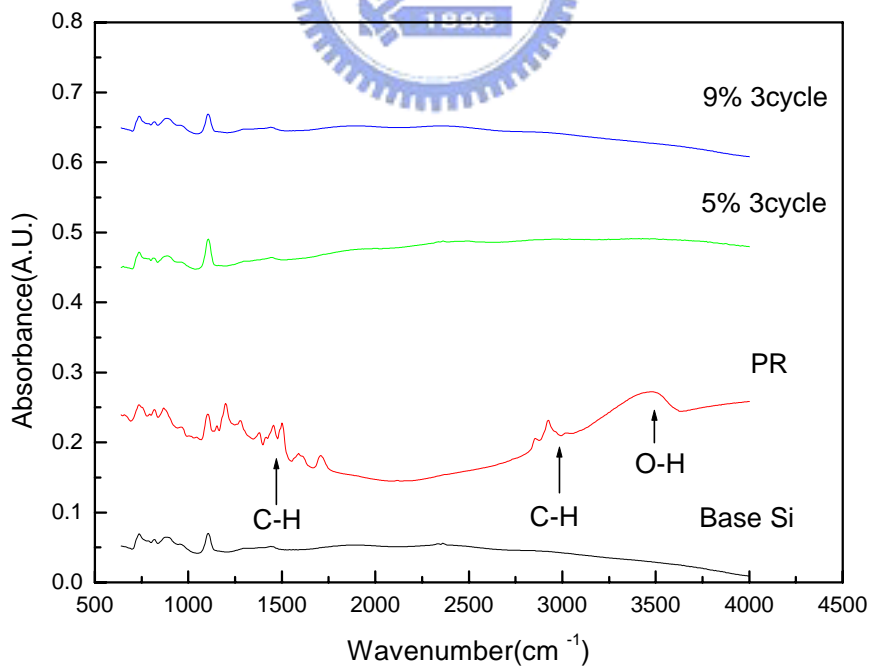


Fig 2-7-2 FTIR spectrum of photoresist stripping on bare silicon by supercritical CO<sub>2</sub> with propyl alcohol

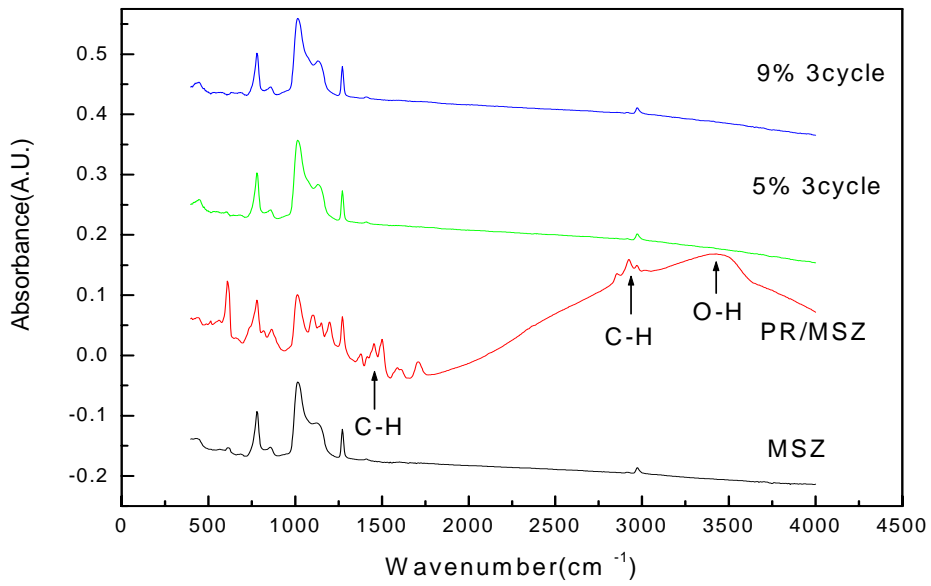


Fig 2-7-3 FTIR spectrum of photoresist stripping on MSZ film by supercritical CO<sub>2</sub> with PCO<sub>3</sub>

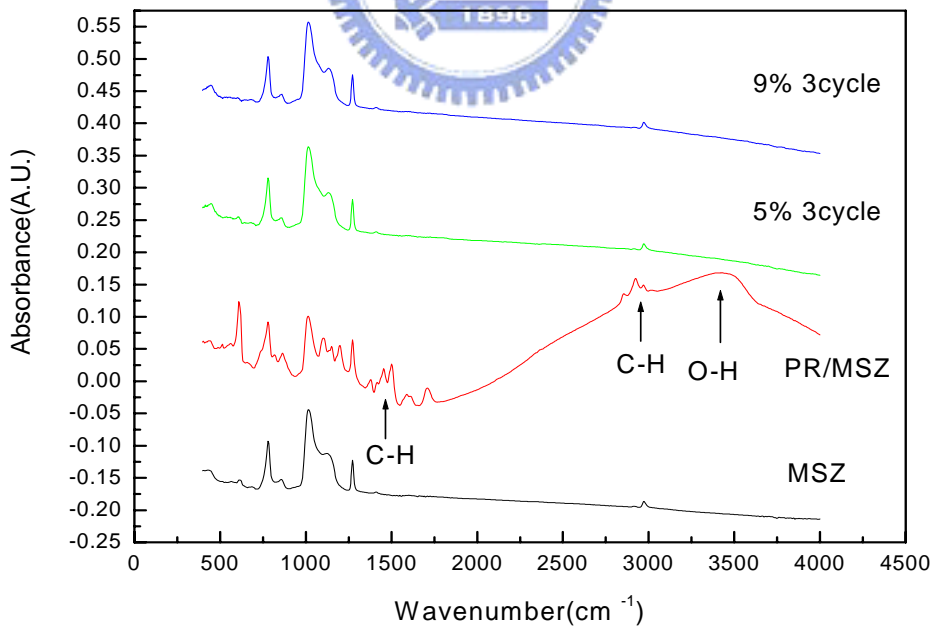


Fig 2-7-4 FTIR spectrum of photoresist stripping on MSZ film by supercritical CO<sub>2</sub> with propyl alcohol

# Chapter 3.

## Study on Process Integration of Low-k MSZ and Supercritical CO<sub>2</sub>

### 3.1 Introduction

Many low dielectric constant materials are under investigation to lower the RC delay of interconnect layers in microelectronic device. Low-k films are patterned using photoresist and Plasma etching followed by ashing with O<sub>2</sub> or other chemistries.

The photoresist and residues are left on the surface of the low-k film after the process, and they must be completely removed to obtain good adhesion.



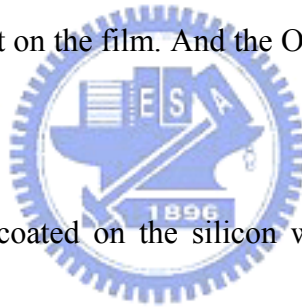
The primary low-k materials for photoresist stripping issues are the selectivity between photoresist and low-k materials, and low-k materials may be mechanically affected. And the low-k films must retain its hydrophobic after the process and each type of low-k film must be fit for the process. There are ongoing effects to improve the Plasma etching process; however the conventional photoresist stripping has a lot of impacts on backend process needed to overcome. So, supercritical CO<sub>2</sub> cleaning process is being investigated for backend applications.

The hard-baked photoresist stripping by supercritical CO<sub>2</sub> is achieved. We can confirm that photoresist stripping by supercritical CO<sub>2</sub> with co-solvent is workable.

Following, the purpose of this work will focus on the supercritical CO<sub>2</sub> impacts of low-k MSZ film.

### **3.2 Experiment Procedures**


In chapter 2, we confirm the photoresist stripping process works. And supercritical CO<sub>2</sub> with 5 % of PCO<sub>3</sub> or propyl alcohol for 3 cycles of process step is needed for the process. The purpose of experiment will focus on the supercritical CO<sub>2</sub> impacts of low-k MSZ film, and the process will act on MSZ film only, lacking of the photoresist on the film. And the O<sub>2</sub> plasma process is the reference of the experiment.



The MSZ solution was coated on the silicon wafer, and bake, hydration, and curing are carried out to form the MSZ film. The parameters are shown as chapter 2. After the standard samples were prepared, some of the samples were treated with oxygen plasma by PECVD. The oxygen gas flow is 300scm, RF power is 300 W, reacted temperature is 300<sup>0</sup>C, and chamber pressure is 300 mTorr, with various treated time :0.5, 1, 3, minutes. The thickness of the MSZ film was measured by n&k analyzer. Material analysis such as Fourier transform infrared spectrum (FTIR) and thermal desorption spectrometer (TDS) are used to confirm the physical and chemical characterization. And the electrical properties will be analyzed.

The MSZ films were soaked with solvents in the air, in order to analyze the effects on the MSZ films. The MSZ samples were soaked with  $\text{PCO}_3$  and propyl alcohol for 3, 6, 9 min. And FTIR and TDS are used to analyze the physical and chemical characterization. And the electrical properties will be analyzed.

The MSZ samples lacking of photoresist were performed for the photoresist stripping process by supercritical  $\text{CO}_2$  with co-solvents. In the experiment, the impact made on MSZ film by the process could be confirmed. The MSZ samples were treated by supercritical  $\text{CO}_2$  with 1%, 5%, 9% of  $\text{PCO}_3$  and propyl alcohol for 3 cycles of process step and dry step. And FTIR and TDS are used to analyze the physical and chemical characterization. And the electrical properties will be analyzed.



In electric study, the metal/insulator/semiconductor (MIS) structure was prepared. Al film was deposited by thermal evaporation as the top and backside electrode. The thickness of Al films are 400nm. After the accomplishment of preparation of MIS capacitors, we performed electrical measurement. There are including Capacitance-Voltage characteristics measured at 1MHz by Keithley Model 82 CV meter, and different temperature measurement and BTS (bias-temperature-stress) for the current-voltage (I-V) measurement by HP4156.

### 3.3 Results and Discussion

Fig 3-1 shows FTIR picture of the MSZ after different  $\text{O}_2$  plasma treatment. The



intensities of Si-OH and H<sub>2</sub>O bonds (933,~3400 cm<sup>-1</sup>) increased gradually when the time of the O<sub>2</sub> plasma treatment is raising. The intensities of C-H bond (2974 cm<sup>-1</sup>), and Si-CH<sub>3</sub> bonds (781, 1273 cm<sup>-1</sup>) decreased after the O<sub>2</sub> plasma treatment. The variation of the spectrum is not obvious, because the bonds of the MSZ film are strong to reduce the damage from O<sub>2</sub> plasma treatment. And the slightly increase in Si-OH and H<sub>2</sub>O bonds is assumed that the dangling bonds generated by O<sub>2</sub> plasma treatment easily absorb moisture when the sample is exposed to the environment. And the oxygen radicals can react with a large number of Si-CH<sub>3</sub> groups on MSZ films, which cause the content of C-H and Si-C bonds decreasing. The reaction will convert Si-CH<sub>3</sub> bonds into Si-OH groups after the reaction. This indicates that after O<sub>2</sub> plasma treatment it will result in moisture uptake. And Fig 3-2 shows that damage of MSZ surface and moisture absorption will increase the dielectric constant, and the leakage current increases with the increase of O<sub>2</sub> plasma treatment time.

Fig 3-3 shows FTIR picture of the MSZ soaked with different solvents and treatment time. And Fig 3-4 shows FTIR picture of the MSZ treated by supercritical CO<sub>2</sub> with 5 % of PCO<sub>3</sub> and propyl alcohol. We find that Si-OH and H<sub>2</sub>O bonds change unobvious. It seems that solvents and supercritical CO<sub>2</sub> process damage the MSZ film slightly, and it needs another evidence to support the hypothesis.

Fig 3-5 shows the electrical properties of the samples soaked with PCO<sub>3</sub> and

propyl alcohol. The electrical properties of the samples are not related to the time of soaking. It seems that the electrical properties depend on the residues of solvents, and are not related to the soaking time.

The electrical properties of the MSZ treated by supercritical CO<sub>2</sub> with PCO<sub>3</sub> and propyl alcohol are shown in Fig 3-6. The leakage current densities of different percent of co-solvents are similar, and it implies that supercritical CO<sub>2</sub> and co-solvents do not impact on the MSZ film. After the treating, MSZ films were baked in a quartz furnace at 200<sup>0</sup>C for 1 hour under N<sub>2</sub> ambient, the dielectric constant does not reduce. It means that after the MSZ films were treated by 3 cycles of process step with PCO<sub>3</sub> or propyl alcohol and by dry step, the moisture on the MSZ films were similar to the STD MSZ, and the furnace treatment is not needed for the process. Besides, both dielectric constant and leakage current are lower than that of O<sub>2</sub> plasma treatment.

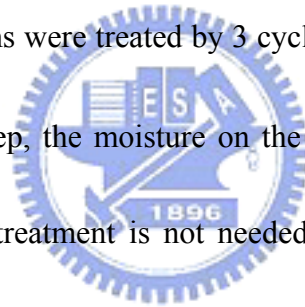


Fig 3-7 shows the TDS moisture desorption spectra picture of MSZ treated by different process. This indicates that O<sub>2</sub> plasma treatment will result in moisture uptake. And the TDS moisture desorption spectra picture of MSZ treated by supercritical CO<sub>2</sub> with 5 % of PCO<sub>3</sub> and propyl alcohol are similar to the STD MSZ. It means that the moisture and solvents are removed by dry step, and it is expected in the process. In the TDS measurement, MSZ samples soaked by solvents can not be measured. It means that moisture and solvents will not be removed completely after

the samples are soaked by solvents.

And the comparison of different process of the MSZ films is done in Fig 3-8.

Compared with the soaking process or the supercritical CO<sub>2</sub> process, the leakage current density and dielectric constant of O<sub>2</sub> plasma process are elevated seriously.

Fig 3-9 shows leakage current densities of MSZ with O<sub>2</sub> plasma process 60 sec and MSZ with supercritical CO<sub>2</sub> process treatment. After 3MV/cm, R.T. 1000 s BTS, the

leakage current densities all increase, however the leakage current density of MSZ with O<sub>2</sub> plasma treatment increases obviously, because of the damaged and moisture

absorption property of MSZ film. According to the result, we know that with increasing O<sub>2</sub> plasma time, the leakage current density increases. However, the

soaking and supercritical CO<sub>2</sub> process will damage the MSZ film slightly, and the leakage current density and dielectric constant increase unobviously than that of

O<sub>2</sub> plasma process.

Fig 3-10 shows leakage current densities of the samples at R.T. and at 150 °C.

The leakage current densities of the STD MSZ and MSZ after supercritical CO<sub>2</sub> process treatment increase obviously at 150°C, while the leakage

current densities of the MSZ after O<sub>2</sub> plasma process treatment slightly increase. All leakage current densities would increase with increasing temperature, revealing a

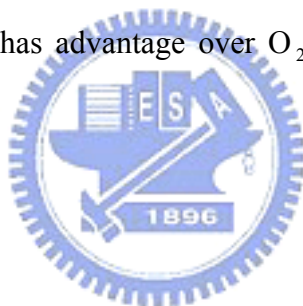
temperature dependence on the leakage behavior. The leakage current density of the

MSZ after O<sub>2</sub> plasma process treatment is higher than the others at R.T. However, the leakage current densities are similar to each other at 150 °C. This means that though the leakage current density increases with increasing temperature, the moisture will be removed at 150 °C and that will cause the leakage current density decreasing. It is the reason why the leakage current density of the MSZ after O<sub>2</sub> plasma process treatment does not increase obviously at 150 °C. Fig 3-11 shows the leakage current densities of each samples on 3MV/cm 150 °C 1000 s BTS, and the leakage current density of the MSZ after O<sub>2</sub> plasma process treatment increases slightly and is similar to the others after BTS at 150 °C.



### 3.4 Summary

In this study, we investigated the effect of various treatments on MSZ film. The results show that MSZ films would absorb moisture after O<sub>2</sub> plasma treatment, and the electrical properties will become worse than STD MSZ. At the same time, the reliability will decrease. The electrical properties of the MSZ films treated by supercritical CO<sub>2</sub> with co-solvent change slightly comparing with STD MSZ, and they are better than that of treated by O<sub>2</sub> plasma obviously. This indicated that supercritical CO<sub>2</sub> with co-solvent is fit for the low k MSZ. Consequently, supercritical CO<sub>2</sub> with co-solvent process has advantage over O<sub>2</sub> plasma process for photoresist stripping in our study.



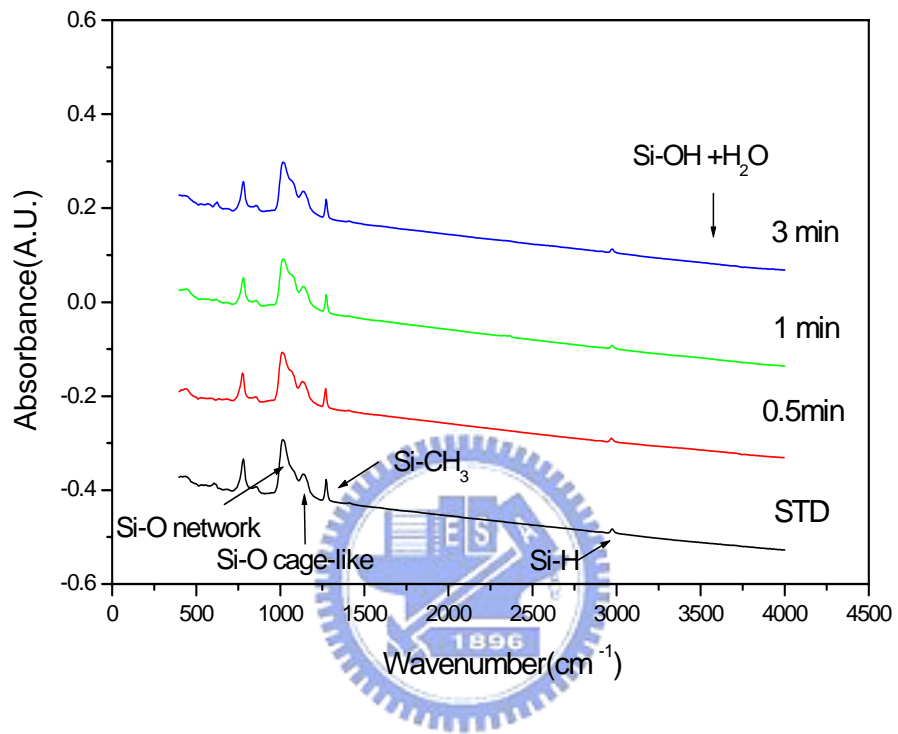


Fig 3-1 FTIR spectra of MSZ with different O<sub>2</sub> plasma treatment condition

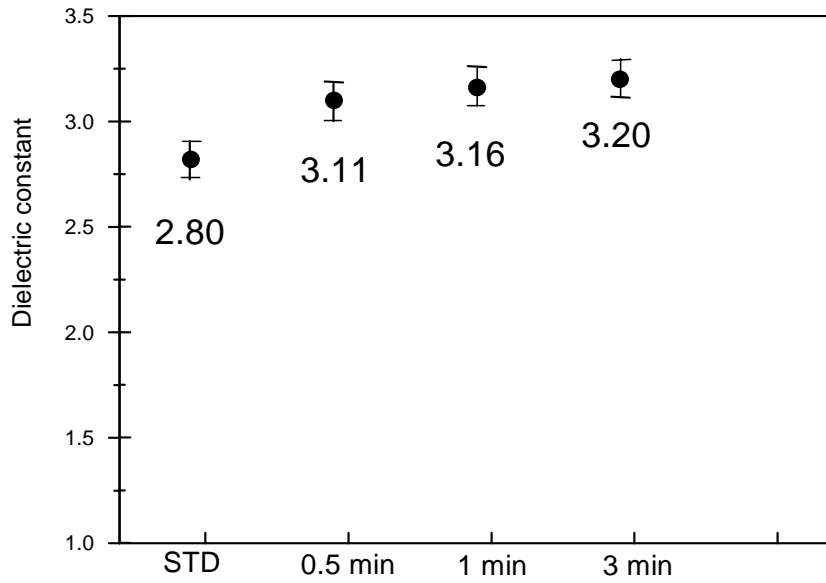


Fig 3-2-1 Dielectric constant variation of different O<sub>2</sub> plasma treatment

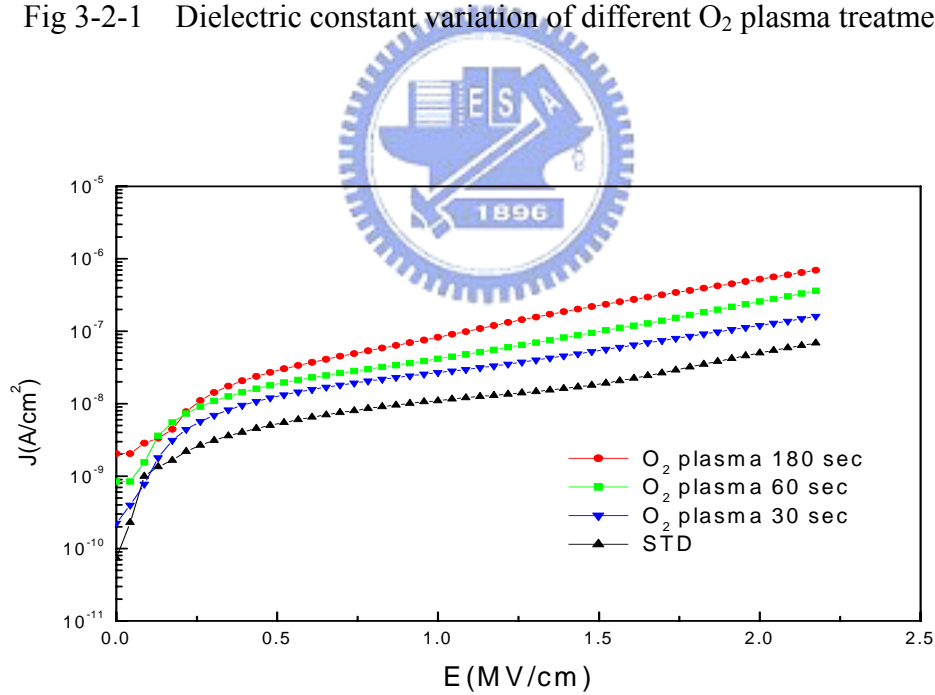


Fig 3-2-2 Leakage current density of MSZ with different O<sub>2</sub> plasma treatment at R.T.

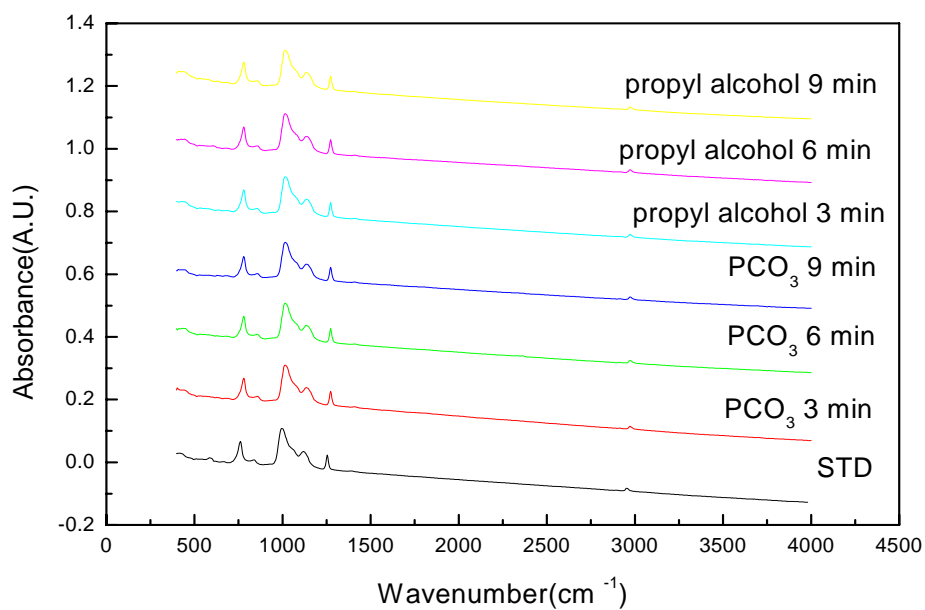


Fig 3-3 FTIR spectra of MSZ soaked with different solvents and treatment time

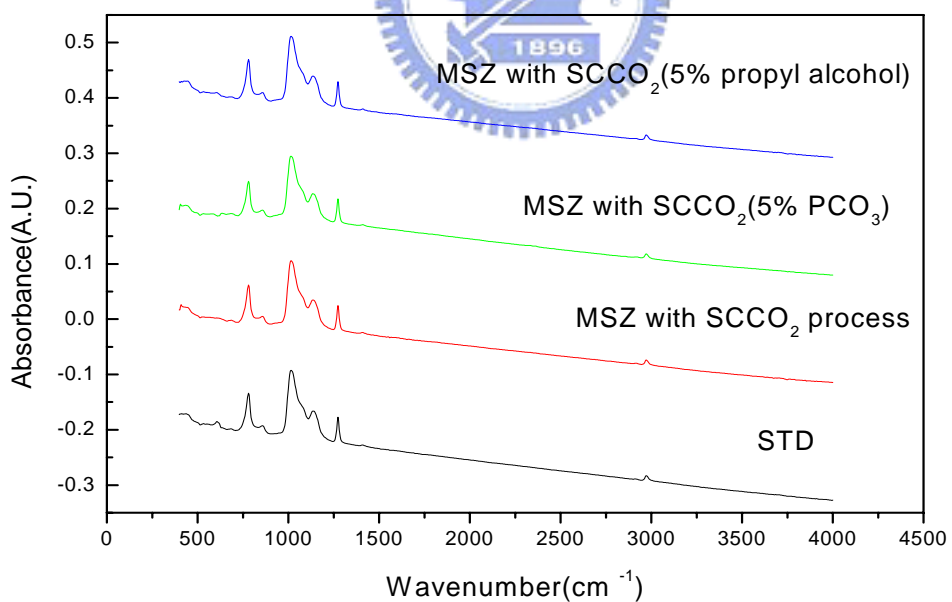


Fig 3-4 FTIR spectra of MSZ treated by SCCO<sub>2</sub> with different cosolvent



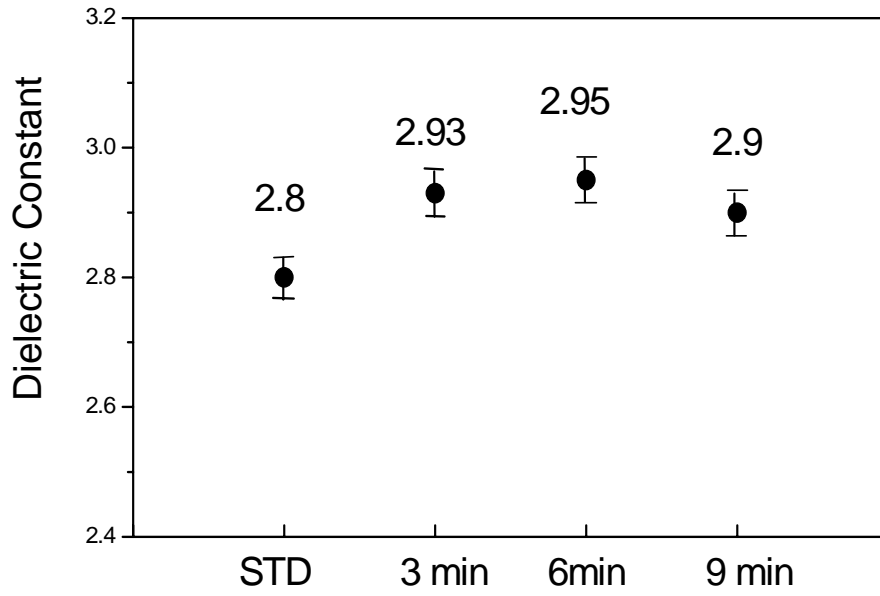


Fig 3-5-1 Dielectric constant of MSZ soaked in  $\text{PCO}_3$

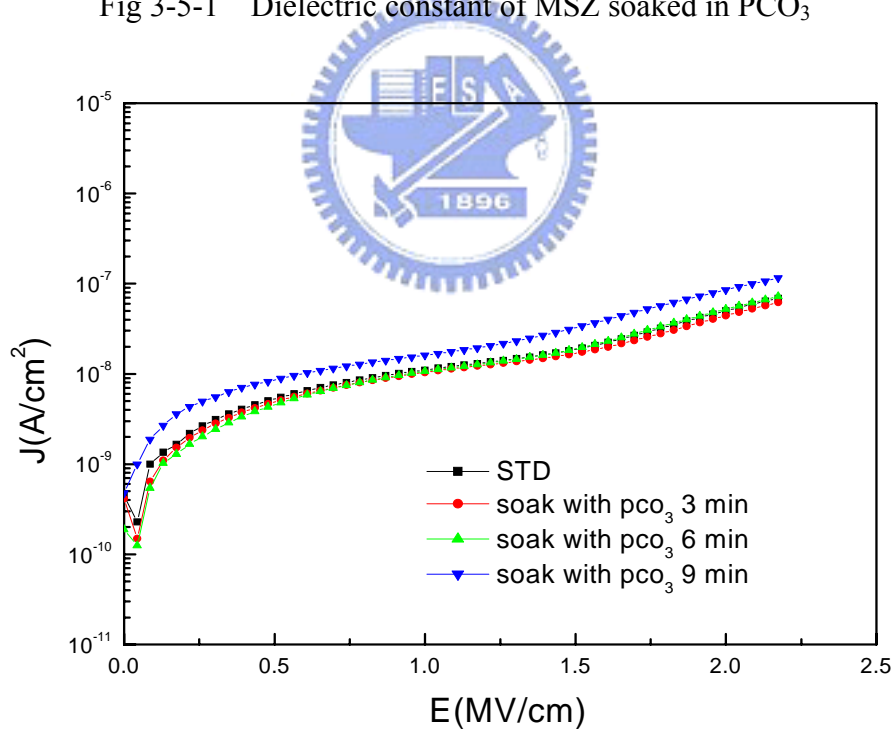


Fig 3-5-2 Leakage current density of MSZ soaked in  $\text{PCO}_3$

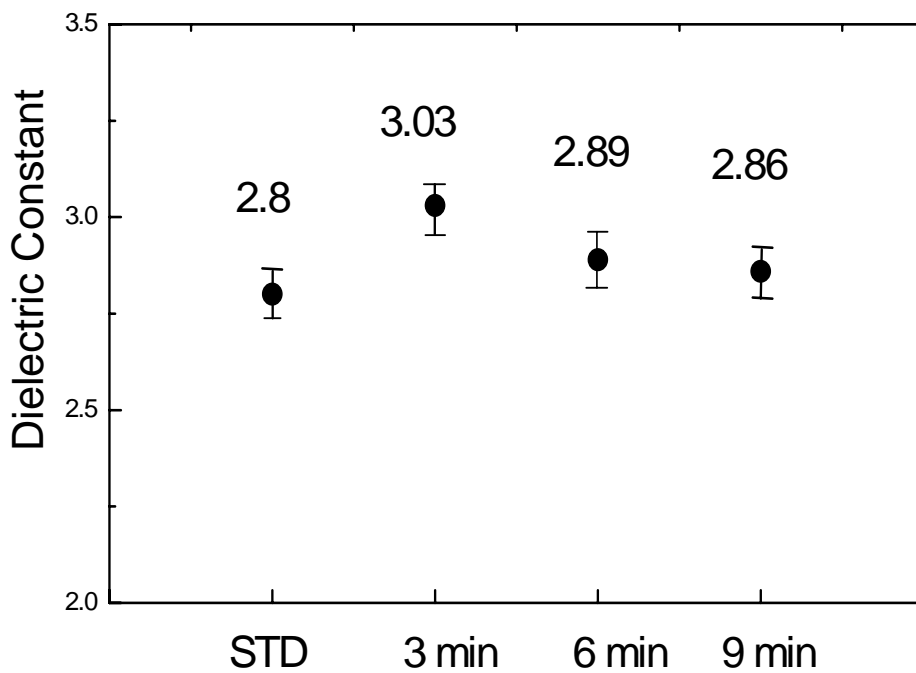


Fig 3-5-3 Dielectric constant density of MSZ soaked in propyl alcohol

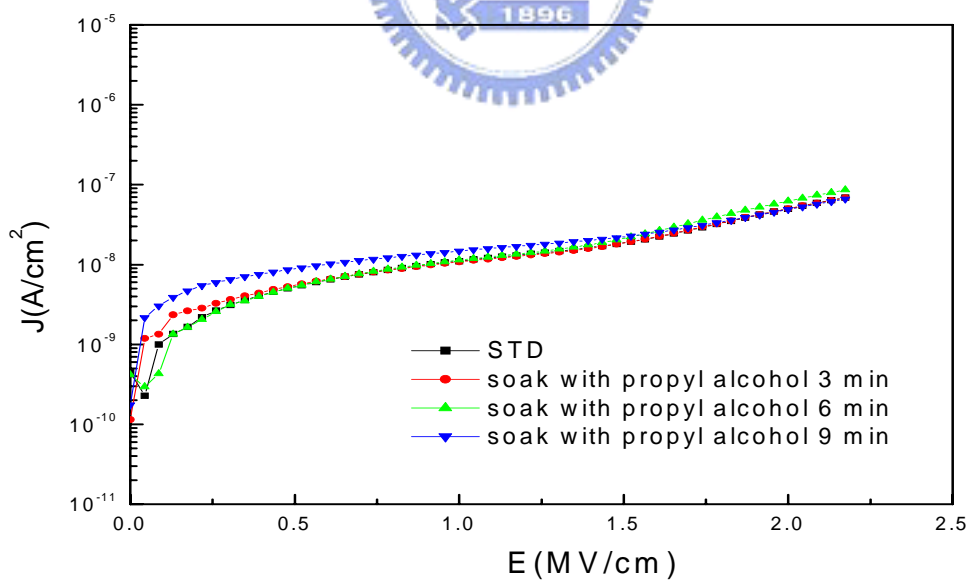


Fig 3-5-4 Leakage current density of MSZ soaked in propyl alcohol

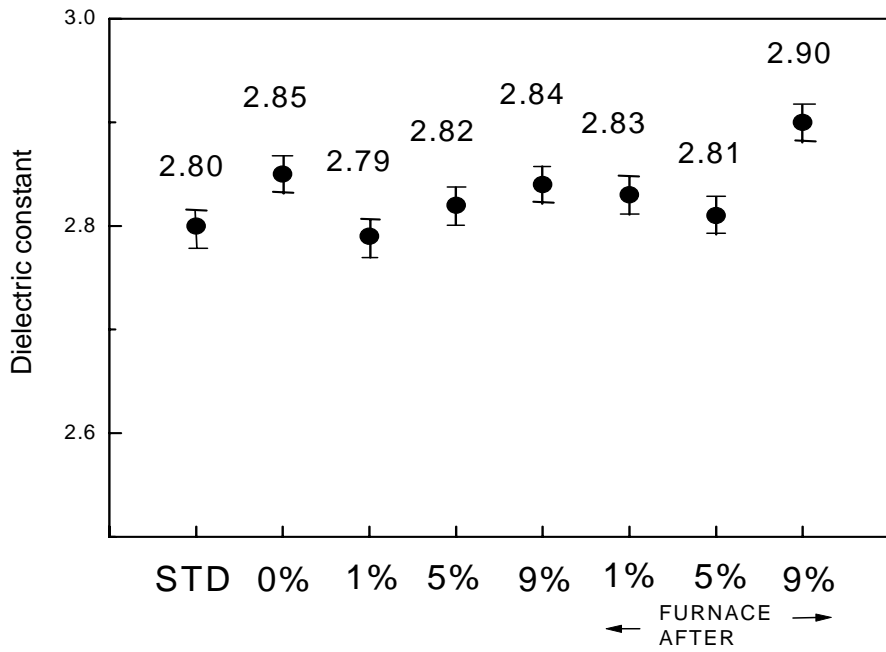


Fig 3-6-1 Dielectric constant of the MSZ treated by supercritical CO<sub>2</sub> with PCO<sub>3</sub>

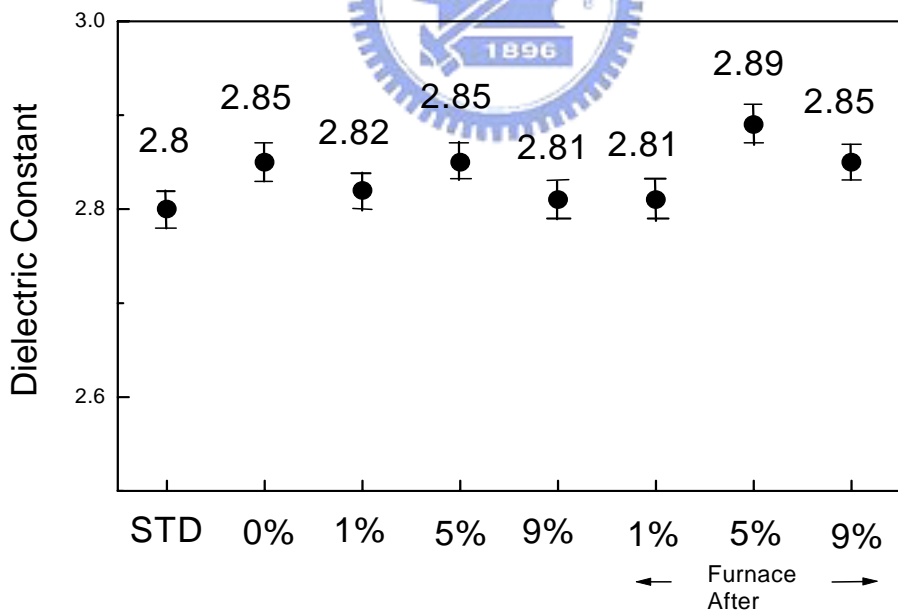


Fig 3-6-2 Dielectric constant of the MSZ treated by supercritical CO<sub>2</sub> with propyl alcohol

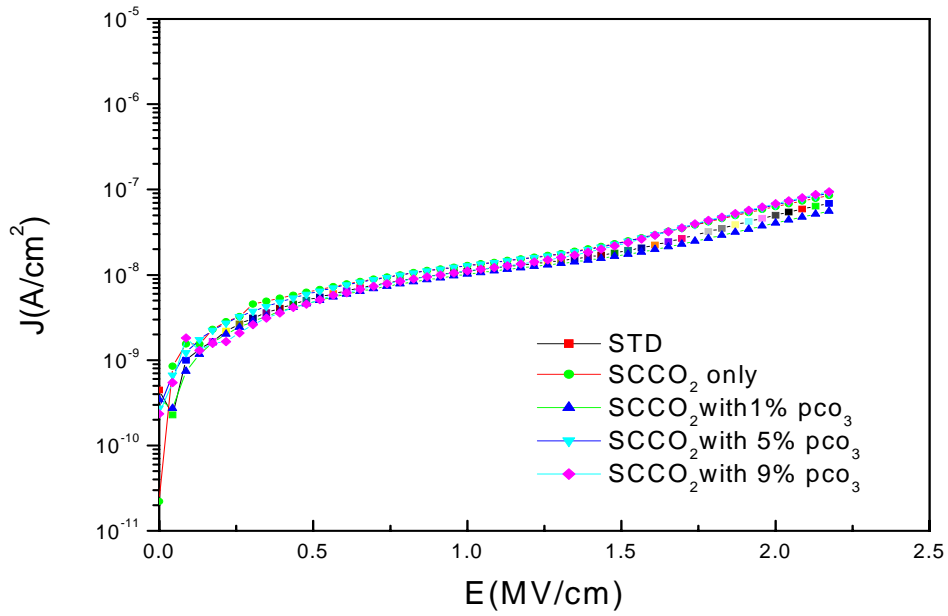


Fig 3-6-3 Leakage current density of MSZ treated by supercritical CO<sub>2</sub> with PCO<sub>3</sub>

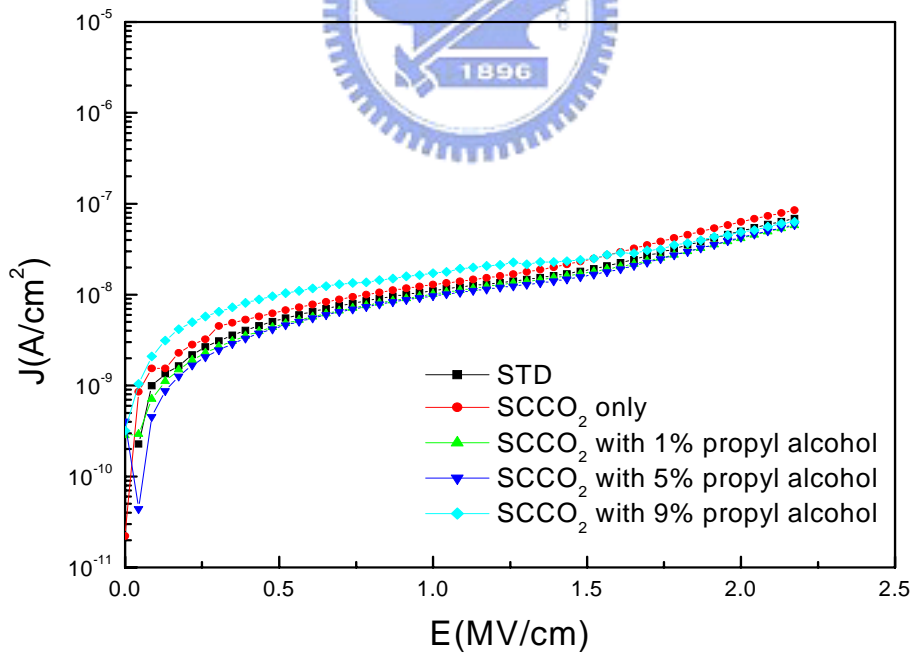


Fig 3-6-4 Leakage current density of MSZ treated by supercritical CO<sub>2</sub> with propyl alcohol

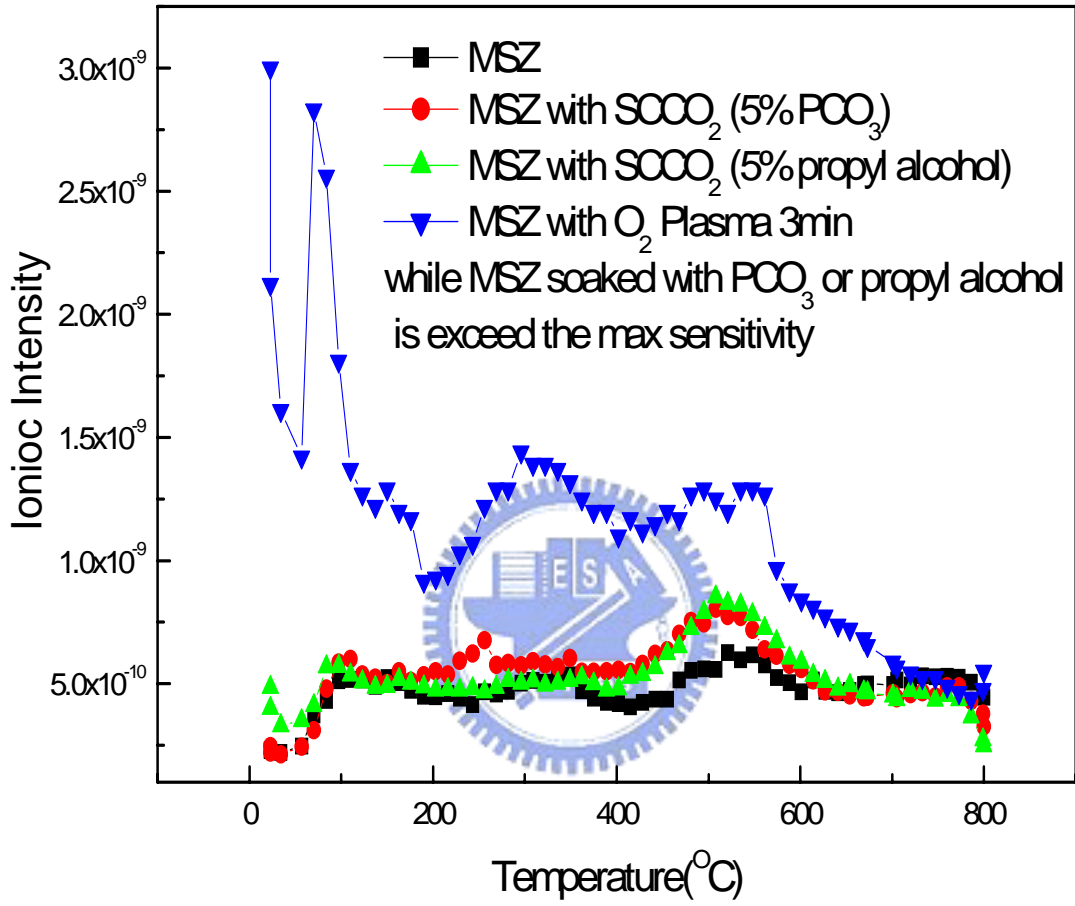


Fig 3-7 TDS moisture desorption spectra of MSZ treated by different process

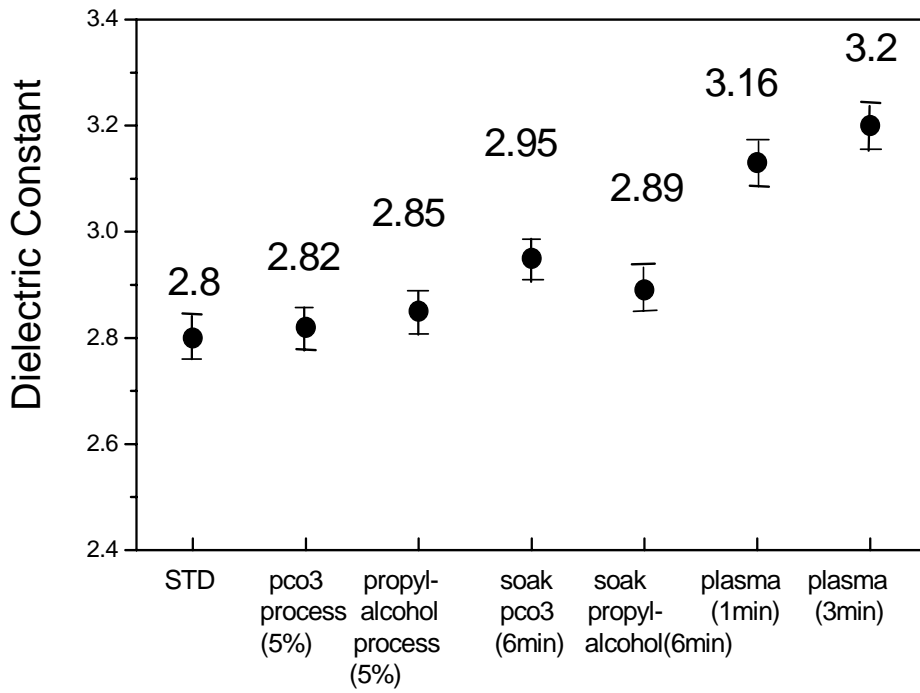


Fig 3-8-1 Total comparison of dielectric constant

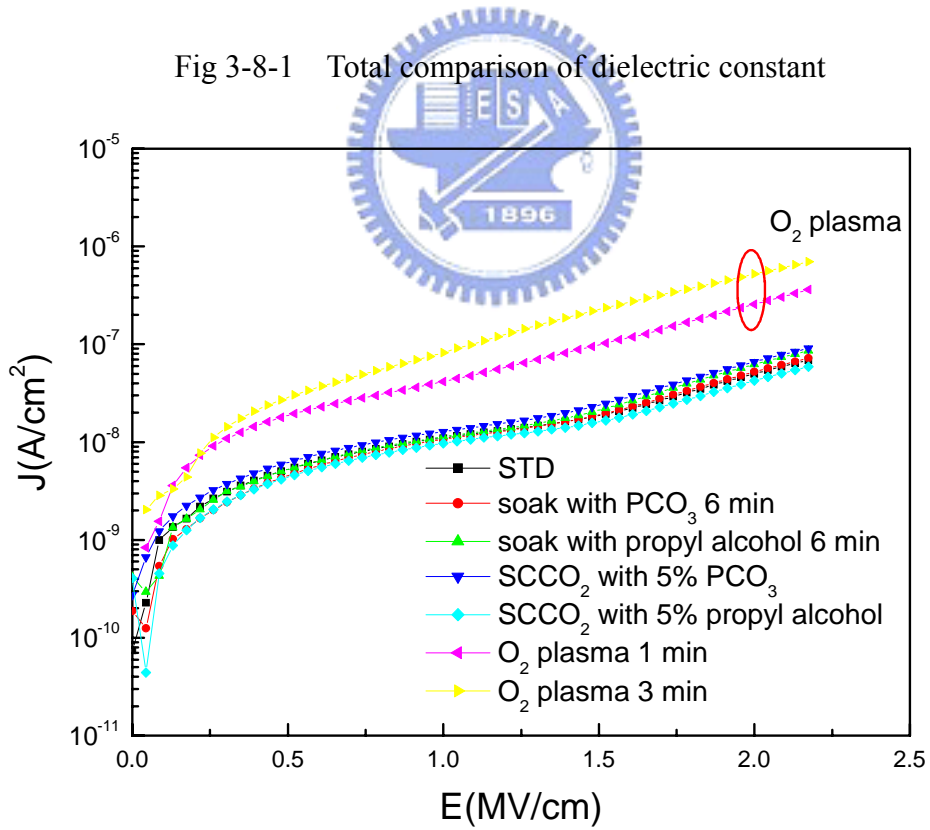


Fig 3-8-2 Total comparison of leakage current density

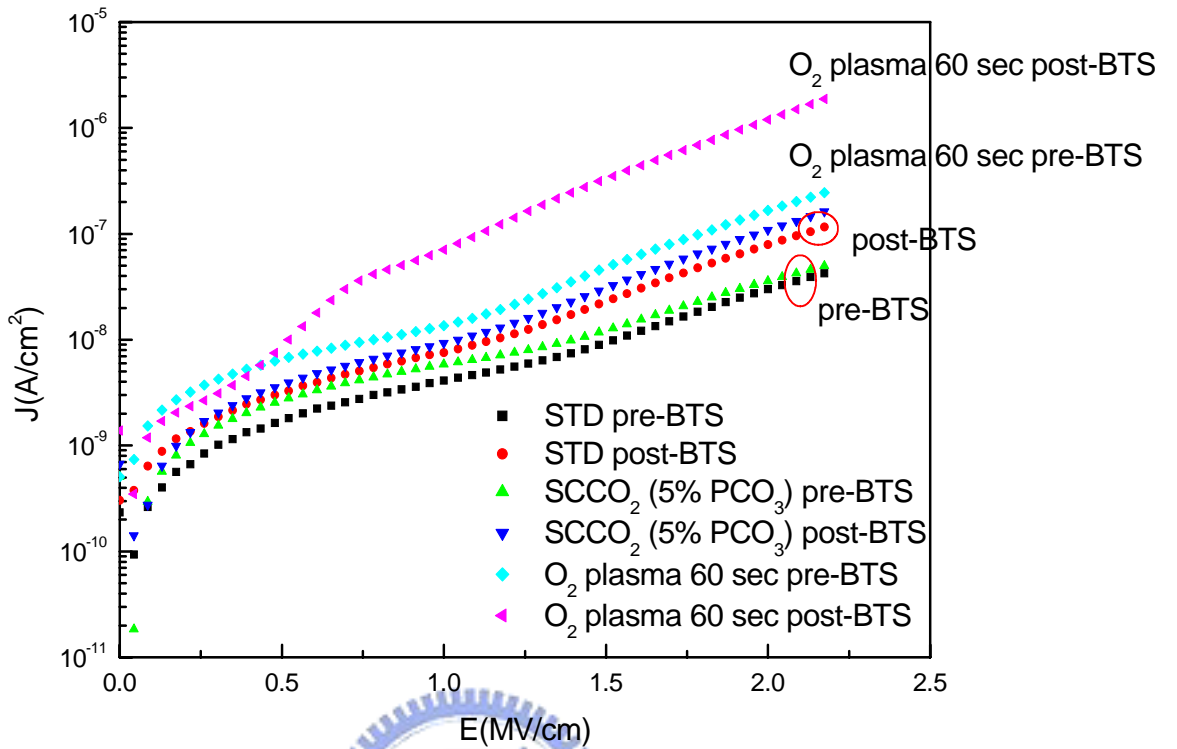


Fig 3-9-1 Total comparison of leakage current density before and after 3MV/cm, R.T. 1000 s BTS

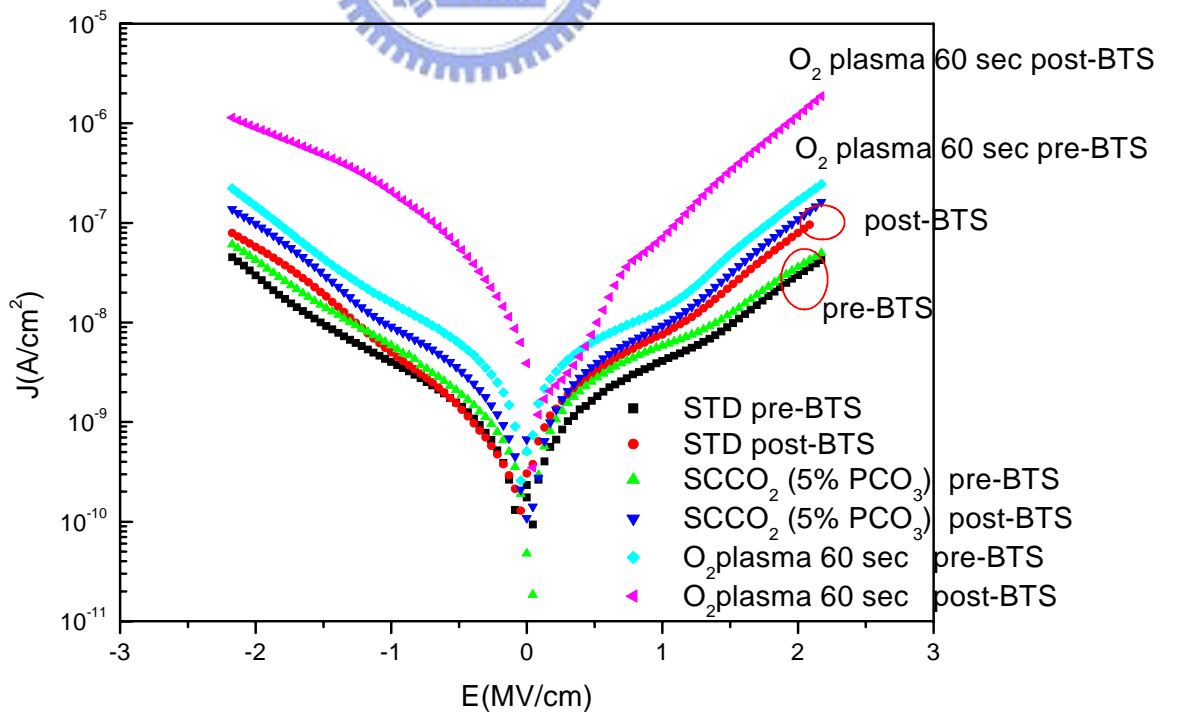


Fig 3-9-2 Total comparison of leakage current density before and after 3MV/cm, R.T. 1000 s BTS

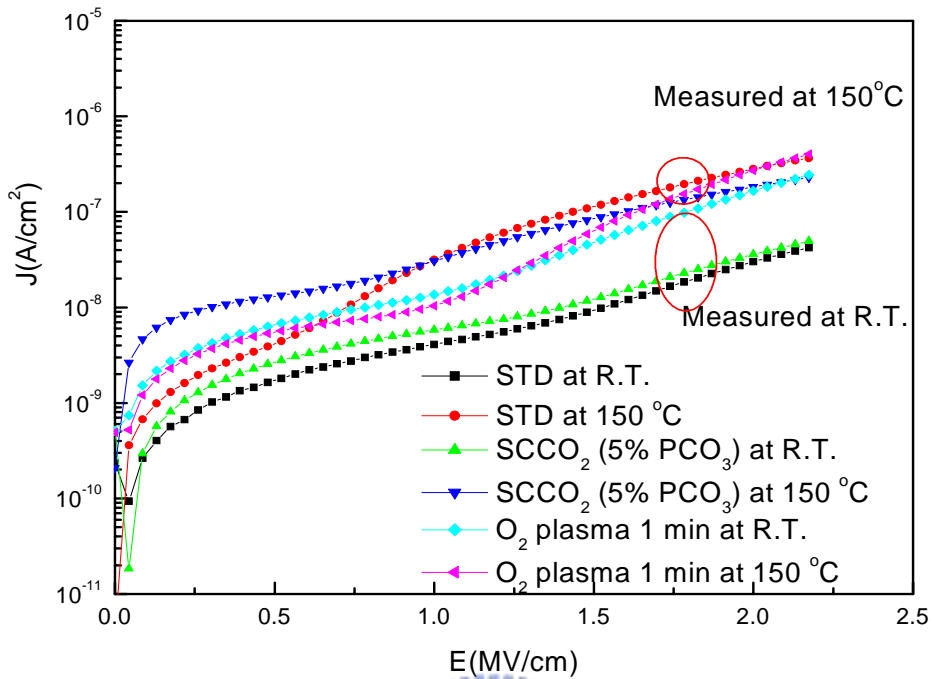


Fig 3-10-1 Leakage current density of the samples at R.T. and at 150 °C.

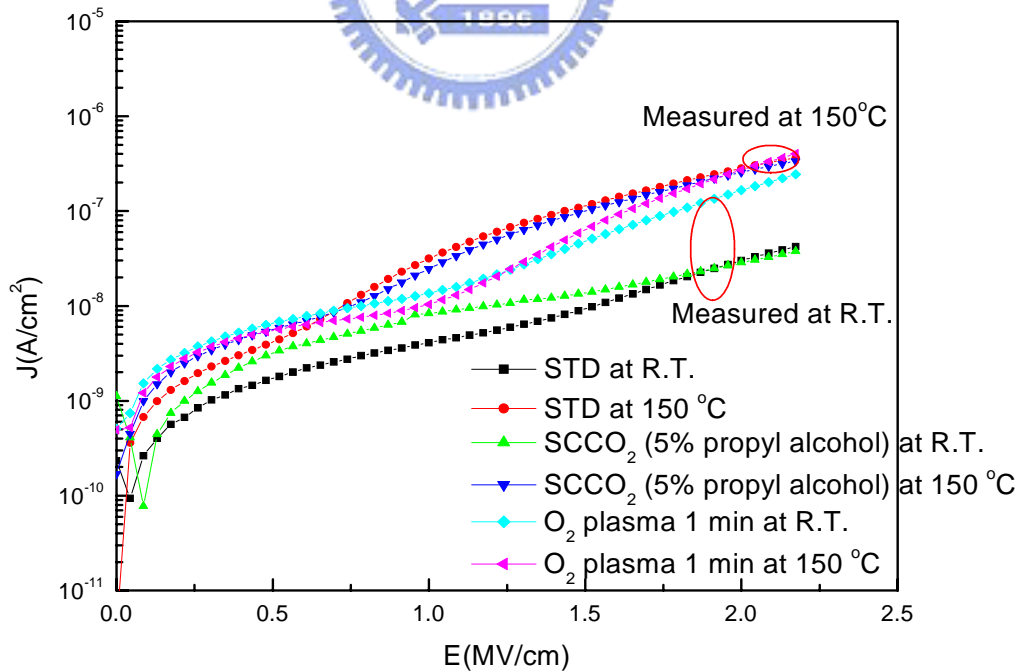


Fig 3-10-2 Leakage current density of the samples at R.T. and at 150 °C.



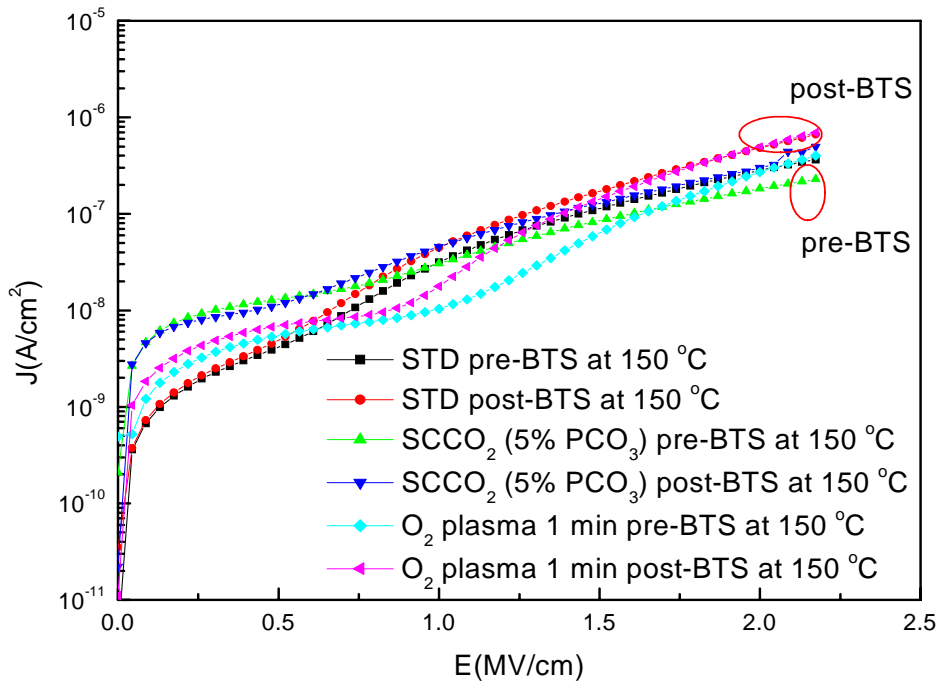


Fig 3-11-1 Total comparison of leakage current density before and after 3MV/cm, at 150 °C 1000 s BTS

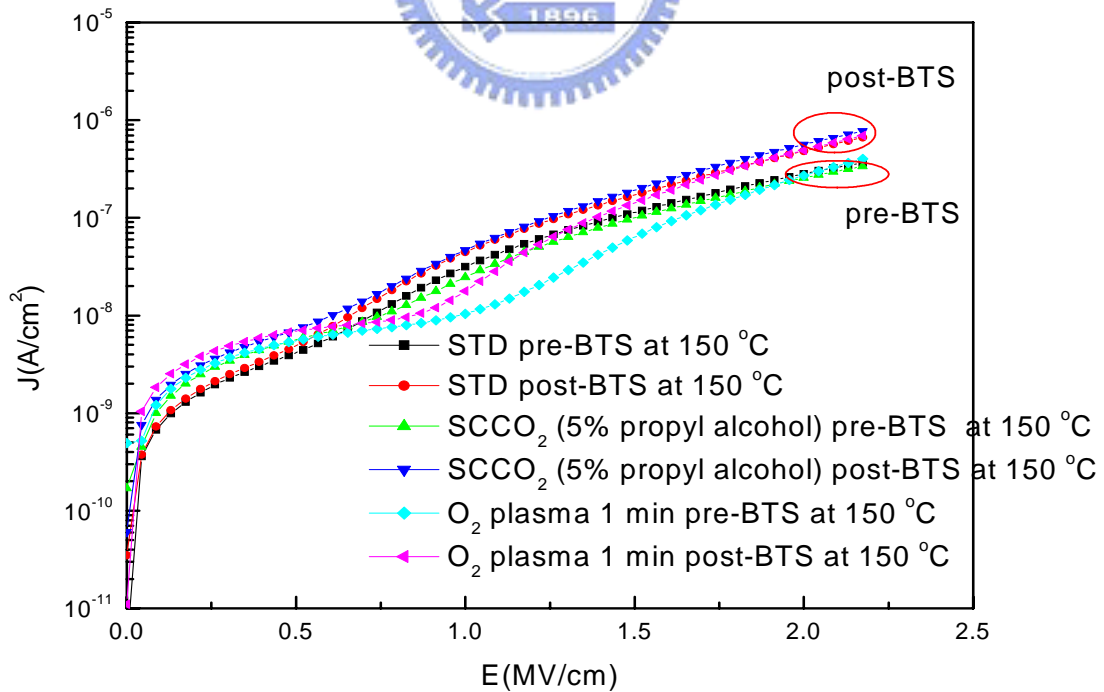


Fig 3-11-2 Total comparison of leakage current density before and after 3MV/cm, at 150 °C 1000 s BTS

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## Conclusions and Future Works

### 4.1Conclusions

In this work, a photoresist stripping process by supercritical CO<sub>2</sub> with co-solvent and its process method are proposed. Overall, the supercritical CO<sub>2</sub> process is effective in stripping photoresist, and it needs less solvents. O<sub>2</sub> plasma ashing is commonly used to remove the photoresist in integrated circuit fabrication. However, O<sub>2</sub> plasma will attack the functional groups of silica-based MSZ films, causing the formation of Si-OH groups during photoresist removal. Comparing with O<sub>2</sub> plasma treatment, supercritical CO<sub>2</sub> with co-solvent has less damage on low k MSZ film. And the electrical properties of MSZ treated by supercritical CO<sub>2</sub> with co-solvent are obviously better than that treated by O<sub>2</sub> plasma. The reliability of MSZ after O<sub>2</sub> plasma treatment during 3MV/cm 1000s BTS at R.T. is worse than the MSZ after supercritical CO<sub>2</sub> process. However, the leakage current density of MSZ after O<sub>2</sub> plasma treatment at 150 °C or during 3MV/cm 1000s BTS at 150 °C is close to that after supercritical CO<sub>2</sub> treatment, because of the desorption of the moisture.

## 4.2 Future Works

In this study, we focus on the photoresist stripping and the impacts on low-k film, and there are numbers of topics relevant to the work which deserve for future studies:

- (1) Investigate the effects of supercritical CO<sub>2</sub> with co-solvent to more low-k materials.
- (2) Remove post-RIE plasma residues on patterned ultra low k films using supercritical CO<sub>2</sub> with co-solvent.
- (3) Remove the Cu metal atoms and CuO<sub>x</sub> contaminations selectively from Cu interconnect lines before deposition of barrier metal.

There are other applications for supercritical CO<sub>2</sub> process. For example, it can be used to deposit metallic and insulating thin films. It is also possible to use supercritical fluids for etching metal and oxide films.

However, the operating conditions require high pressure process chambers not typical found in the vacuum-intensive semiconductor fab. This imposes a psychological safety for the supercritical CO<sub>2</sub> technology.

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