Chapter 2

The Purpose and Method of This Study

2.1 The purpose of this experiment

Lithographic process employes the photoresist to define the regions for the ion implantment and etching process, and then he photoresist has to be removed. The O_2 plasma ashing and wet chemical cleaning are the convenational method for the removal of photoresist and residue after ion implantation and etching process.

As semiconductor device dimensions approach the nanoscale, it will become increasingly difficult to use aqueous-based cleaning processes due to high surface tension and capillary forces. Effective penetration into the high aspect ratio trenches and via structures will be challenging. The rinsing and drying steps will also become more difficult. With the introduction of copper and low-k technolngy however, these convenational ashing/cleaning technologies are being challenged more and more.

Therefore, we will require an innovative technology, significantly different from today’s processes. Supercritical fluids provide the enabling capabilities for overcoming the process barriers encountered as we approach nanoscale dimensions and copper/low-k technology.

2.2 The apparatus for the experiment

The apparatus for this experiment is Isco Supercritical Fluid Extraction System, that consist of an SFX 220 extractor, an SFX 200 controller, and two syringe

pumps. The system after modified is shown as Figure 2, Figure 3, Figure 4, Figure 5.

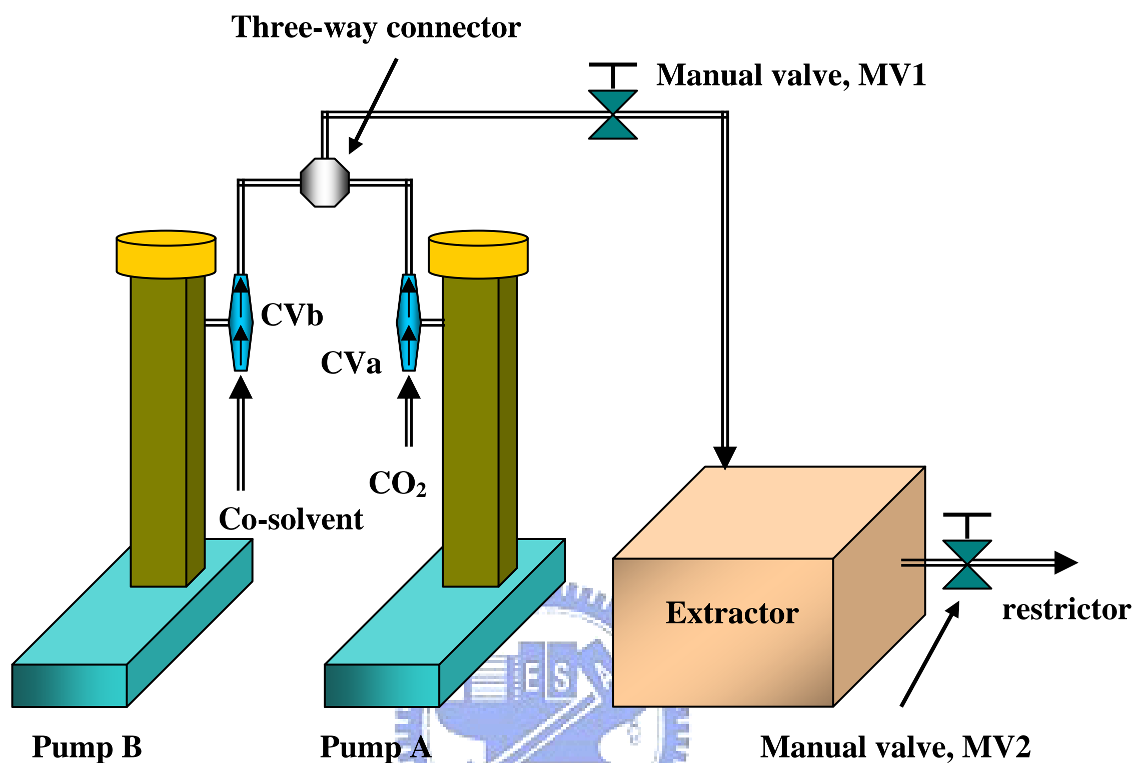


Figure 2 Isco supercritical fluid extraction system (CVa, CVb are one-way valve)

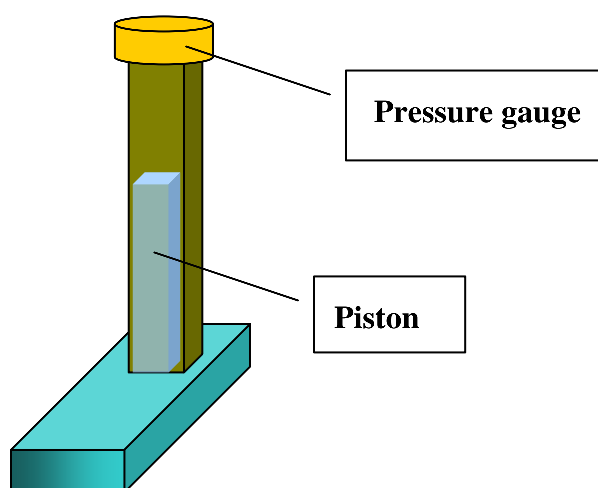


Figure 3 Syringe pump

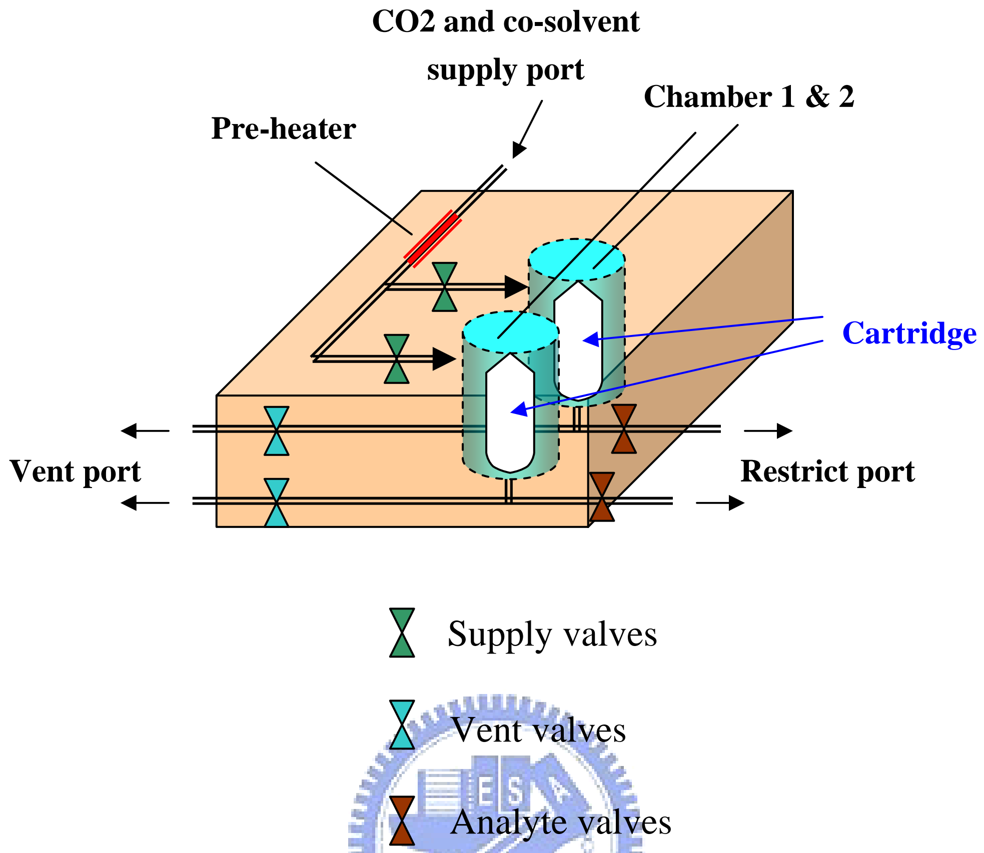


Figure 4 The structure of extractor inside

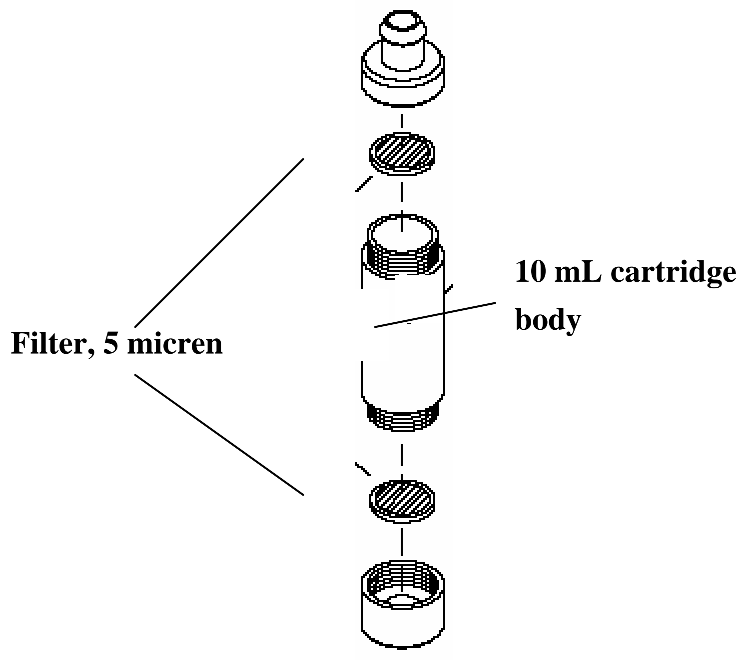


Figure 5 Cartridge

2.3 The purpose of this experiment

The purpose of this experiment is studing the removal of photoresist and residue after silicon dioxide etching using supercritical carbon dioxide and co-solvent. The co-solvent is a solvent mixture of PCO3（propylene carbonate）and DMSO（dimethyl sulfoxide）, the proportion of PCO3 and DMSO is 1:1. The type of photoresist for this experiment is positive photoresist for I line process（THMR-iP3650 HP）.

Why is the “PCO3＋DMSO” as a co-solvent in this experiment

（1）The 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-solvent can be added to enhance the solubility of polar materials, similar to photoresist.

（2）Referring to the literature “A Comparsion of DI Water/Ozone and CO_2-Based Supercritical Fluid as Replacements for Photoresist-Stripping Solvents” [8]. The PCO3（propylene carbonate）is a polar organic solvent, and that can be added to enhance the solubility of photoresist in the supercritical carbon dioxide.

（3）Referring to the literature “ Removal of photoresist and residue from substrate using supercritical carbon dioxide process ” [9]. The DMSO（dimethyl sulfoxide）also can be added to enhance the solubility of photoresist in the supercritical carbon dioxide. Furthermore, the DMSO is a dipolar organic solvent.

So we assume that small amounts of DMSO can be added to enhance the solubility of PCO3 in supercritical carbon dioxide, and thus, there are more amounts of PCO3 and DMSO can be carried by the supercritical carbon dioxide and infused into the photoresist.

The experiment is divided into three stages, and the description as following:

2.3.1 The first stage

The removal of post-hard bake photoresist on bare silicon wafer, the photoresist coating consist of （1）Dip for removed the native oxide with a mixture of HF and H_2O.（2）Coating HMDS.（3）Coating photoresist（8000Å）.（4）Soft bake at 90℃, 90 second.（5）Post-exposure bake at 110℃, 120 second.（6）Hard bake at 120℃, 90 second. Following the photoresist coated, the wafer is cut for form the samples, and the sample dimension is 4 cm × 1 cm.

2.3.2 The second stage

The removal of post-ion implantation photoresist on bare silicon wafer, the procedure of photoresist coating is the same as the first stage. Following photoresist coated, the ion implantation process is performed. The ion dose is 5×10^{15} cm^{-2}, ion energy is 100 KeV. Following ion implantation, the wafer is cut for form the samples, and the sample dimension is 1 cm × 1 cm.

2.3.3 The third stage

The removal of photoresist after silicon dioxide etching process. The thickness of silicon dioxide is about 5500Å, and the pattern consist of lines and pillars . The

lithograohy process consist of (1) Coating HMDS. (2) Coating photoresist. (3) Soft bake at 90℃, 90 second. (4) Exposure. (5) Post-exposure bake at 110℃, 120 second. (6) Development. (7) Hard bake at 120℃, 90 second. Following the lithography, the silicon dioxide etching process is performed, and then the wafer is cut for form the samples. The sample dimension is 1 cm × 1 cm.

2.4 The method for this experiment [4]

Refering to Figure 6 [4], the sequence of removing method consists of 6 basic process steps :

2.4.1 Load, Purge, Pressurize chamber

1. Load, putting a sample into the cartridge, then putting the cartridge into the chamber, and sealed chamber.

2. Purge, when the pressure set value (1100 psi) of pump A and pump B are arrived, and the system is equilibrium, then opening the manual valves (MV1 and MV2). The chamber is purged with a continuous flow of the mixture of supercritical carbon dioxide and co-solvent to replace the air that is trapped in it.

3. Chamber pressurization, the manual valve (MV2) is closed, the chamber is then charged with the mixture of supercritical carbon dioxide and co-solvent and pressurized to a pressure of 1100 psi. The manual valve (MV1) is closed when the pressure in chamber reached 1100 psi.

2.4.2 Fill chamber

1. The pump pressure is preseted to the desired operating pressure P_0. Once the pump pressure has reached P_0, and the system equilibrium is arrived. The manual valve（MV1）is opened, and then the mixture of supercritical carbon dioxide and co-solvent inject into the chamber.

2. Once the chamber pressure has reached P_0, the manual valve（MV1）is closed, and began the Soak step.

2.4.3 Soak

1. During the Soak period, the infusion of carbon dioxide and co-solvent at high pressure into the photoresist and sidewall polymer material causes swelling.

2. During this swelling process mechanical stress occurs at the interface of the photoresist and polymer material to the substrate, tending to stress, weaken, and rupture the interface bond at a microscopic level.

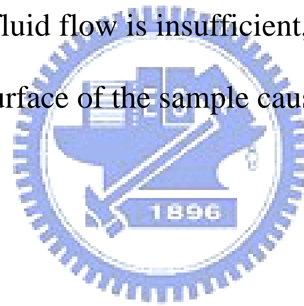
3. The co-solvent during the soak step to weaken and break chemical bonds within the polymer layer of the bulk photoresist reducing its average molecular weight. The soak step is static with no flow.

2.4.4 Agitation and Flush

1. Agitation, when the soak step han finished, the manual valve（MV2）is opened to apply rapid decompression to the chamber（P_1）. By application of the rapid decompression step, the photoresist and sidewall polymer material having been

previously infused with carbon dioxide and co-solvent under the higher pressure P_0 during the soak step, is now subjected to a dramatic stress of interal and external pressure differential, inducing a mechanical rendering, breaking up and loosening of the structure of the photoresist and sidewall polymer as the carbon dioxide and co-solvent is evacuated.

2. Flush, once the pressure in chamber is dropped to P_1, the manual valve（MV1）is opened to introduce an inflow at P_1 that will sustain the rate of outflow, thus providing a full flow washing action through the chamber over the sample to lift and flush the loosened and lossening material during the decompressive rendering. The flush step has to be sufficient fluid flow to remove the debonded photoresist and polymer. If the fluid flow is insufficient, the debonded photoresist and polymer will remain on the surface of the sample cause contamination.



2.4.5 Rinse

1. The rinsing step is performed to remove the residue and co-solvent after flush step.

2. If the agitation and flush steps are finished, then the manual valve（MV2） is closed causing the pressure in the chamber rise to P_0, beginning the subsequent step, rinse step, at full pressure and full flow.

3. Rinsing can be performed either in the liquid or supercritical phase with pure carbon dioxide or carbon dioxide and additive, e.g. surfactant.

4. According to the literaturs of “Supercritical fluid cleaning process for precision surfaces”, the complete process of photoresist removal there is a rinse step. But the apparatus of Isco Supercritical Fluid Extraction System could not perform this

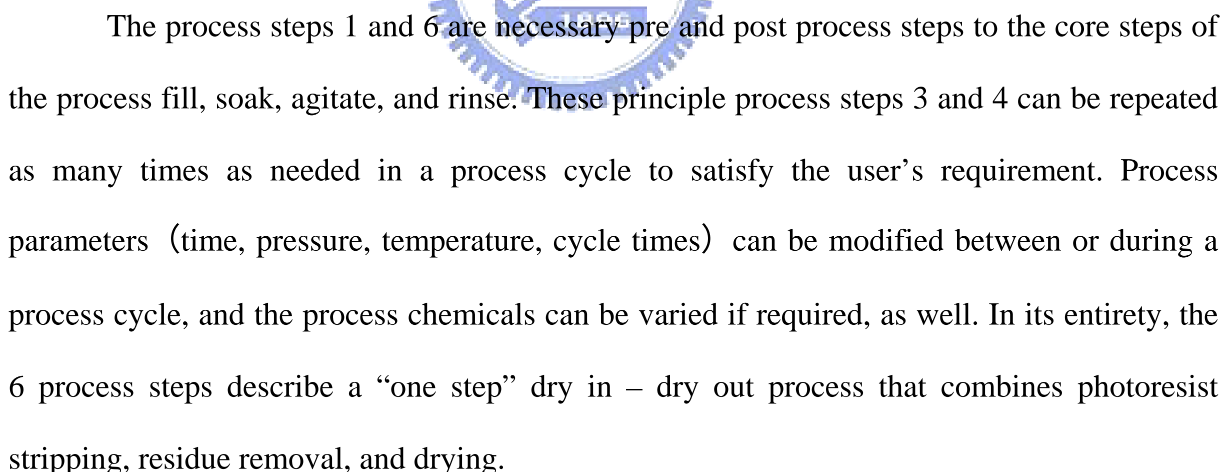
function, and therefore, we perform the DI water rinsing in place of the rinse step with carbon dioxide and additive.

2.4.6 Dry, Vent, Unload

1. To dry the sample with supercritical carbon dioxide by maintaining the chamber at higher temperature than supercritical temperature when decreasing chamber pressure to ambient without entering a liquid phase condition.

2. This technique transforms supercritical carbon dioxide directly into the gas phase without crossing the liquid-gas boundary. Residual stains due to liquid droplet formation are prevented.

3. To open the chamber and unloading the sample.



The process steps 1 and 6 are necessary pre and post process steps to the core steps of the process fill, soak, agitate, and rinse. These principle process steps 3 and 4 can be repeated as many times as needed in a process cycle to satisfy the user's requirement. Process parameters (time, pressure, temperature, cycle times) can be modified between or during a process cycle, and the process chemicals can be varied if required, as well. In its entirety, the 6 process steps describe a "one step" dry in – dry out process that combines photoresist stripping, residue removal, and drying.

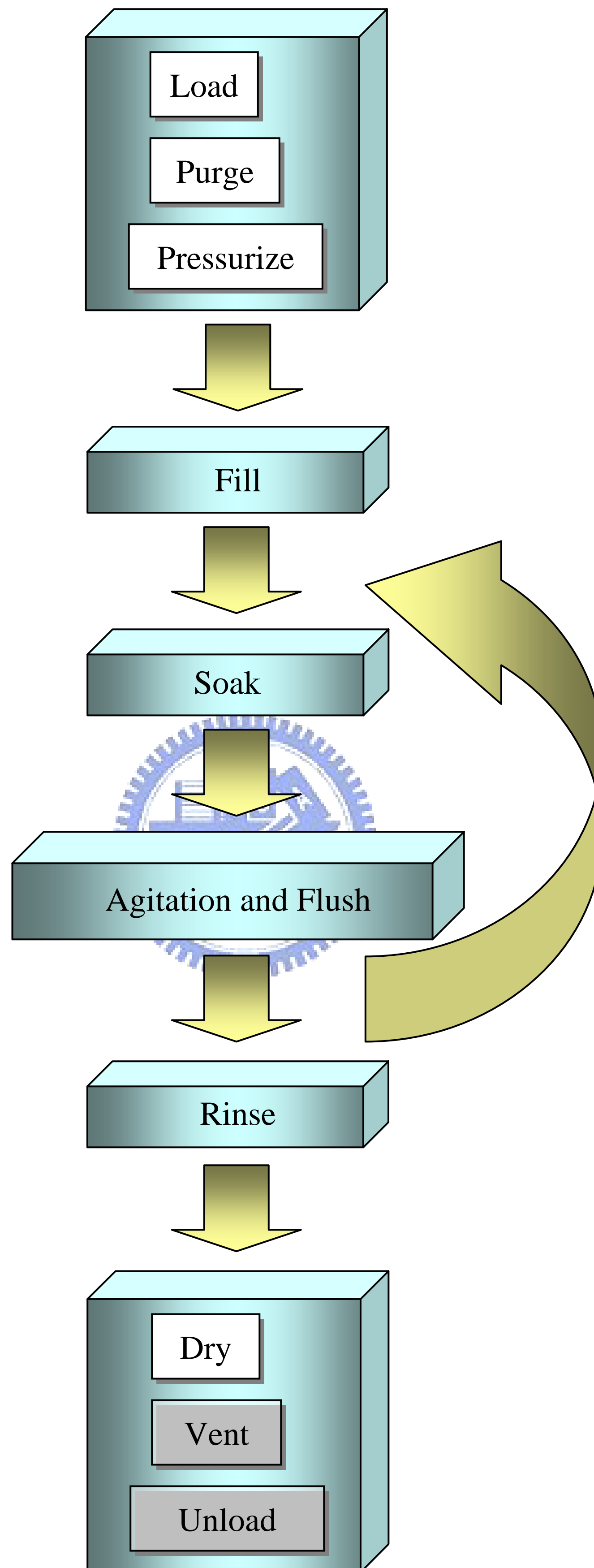


Figure 6 The flowchart of the process sequence [4]