

# EQUIPMENT FOR THE CLEANING OF SILICON WAFERS USING SUPERCRITICAL FLUIDS

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## ABSTRACT

Supercritical CO<sub>2</sub> has some promising applications in integrated circuits manufacturing. In order to evaluate them, a prototype dedicated to the treatment of silicon wafers of 200 mm diameter has been built and is presented here.

## INTRODUCTION

In semiconductor manufacturing, the size reduction of advanced microelectronic devices led to the introduction of new materials for the Back-End Of the Line (BEOL) integration. High performances couple of conductor/insulator materials is requested to produce sub-micronic transistor interconnections. Thus, aluminium is now replaced by copper as conductor in advanced manufacturing, and porous ultra-low K dielectrics (ULK) are investigated as new insulators.

Some integration processes, especially cleaning and stripping (the removal of photosensitive resin and residues following the lithography steps), have shown a detrimental impact on further integration steps and electrical performances of Cu/ULK structures <sup>[1]</sup>. This weakness comes from the fragility of the ULK towards plasmas and liquid-based chemistries. Furthermore, the porosity of ULK materials induces "reservoir" effects and strong diffusion issues.

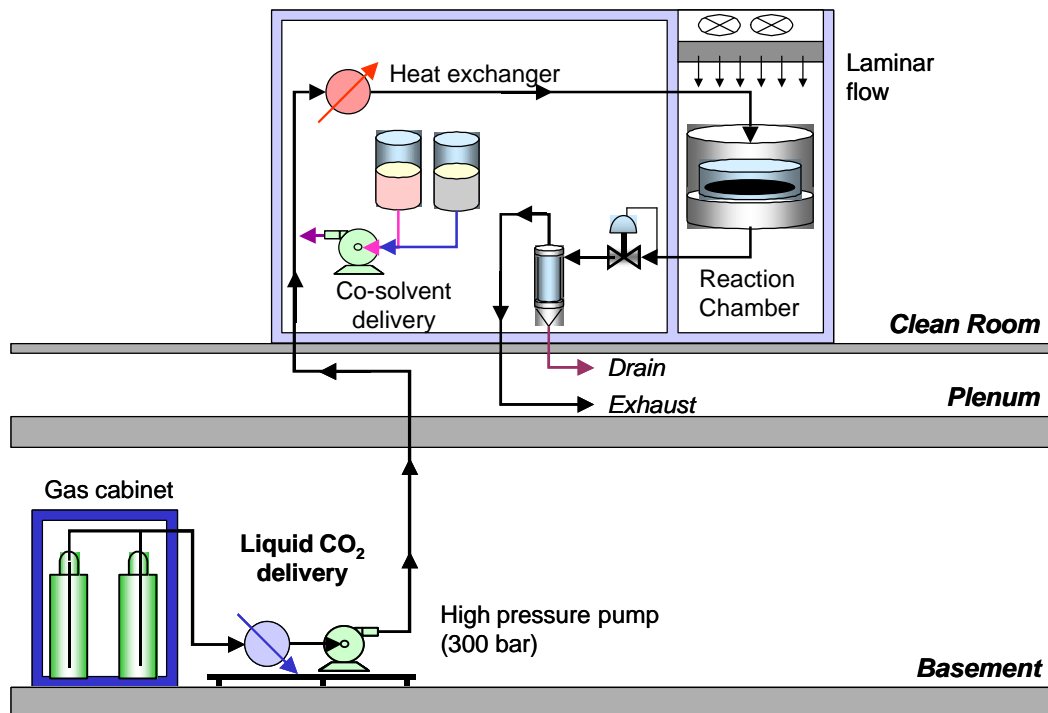
With its unique properties, supercritical CO<sub>2</sub> is one of the most promising alternatives or complements to dry and wet BEOL processes. In order to determine potential benefits and limits of supercritical fluids for semiconductor manufacturing, a prototype has been set-up in CEA-Leti clean room. This equipment has been built under a strong partnership:

- Air Liquide: high purity supercritical CO<sub>2</sub> and co-solvents delivery to the point of use, separation ;
- Separex and Recif: process chamber (autoclave and process functionalities) ;
- CEA-Leti, Altis and Recif are in charge of process development.

## I – EQUIPMENT DESCRIPTION

### *Main Characteristics*

The equipment presented in this work is designed for the evaluation of supercritical carbon dioxide and liquid additives implementation on silicon wafers of 200 mm diameter. A simplified process diagram and set-up is illustrated in figure 1. Pictures 2 and 3 shows the equipment and the wafer loading operation.



**Figure 1:** Supercritical CO<sub>2</sub> process diagram and set-up in CEA-LETI.

CO<sub>2</sub> is continuously supplied by a gas cabinet containing 2 bottles of 50 l, with automated switching. CO<sub>2</sub> is then compressed by a high-pressure pump and sent to the equipment in the clean room. Additives are injected in the high-pressure line before the heating exchanger and the treatment autoclave. This autoclave is designed to receive a single wafer of 200 mm. Its opening and closure are automated. CO<sub>2</sub> is then vented through a flash separator, where residues and additives are recovered and evacuated to solvent disposal.

As very different processes will be evaluated on this equipment, versatility and flexibility have been two priorities for the design of this unit:

- Broad range of pressure and temperature: up to 300 bar and 100°C ;
- Different configurations available for the autoclave inlet and outlet ;
- Versatile recipe programming software ;
- Possibility to implement several mechanical effects to enhance cleaning efficiency ;
- Two liquid additive tanks for multi-step process.



**Figure 2:** Prototype front view



**Figure 3:** Wafer loading in the chamber

### ***Wafer contamination control***

Particles as small as  $0.05 \mu\text{m}$ , metals, ions, and heavy organics are highly detrimental contaminations for advance integrated circuit manufacturing. For this reason,  $\text{CO}_2$  and additives are ultra-pure and particle-free. Moreover, all parts in contact with these fluids have a high quality of finishing and high-purity polymeric materials are selected (no additives such as dyes, which could salt out during process). In addition, filtration is ensured with a retention efficiency of 99.9% at  $0.01 \mu\text{m}$  (for gas), and a laminar flow prevents particle contamination during wafer loading in the autoclave.

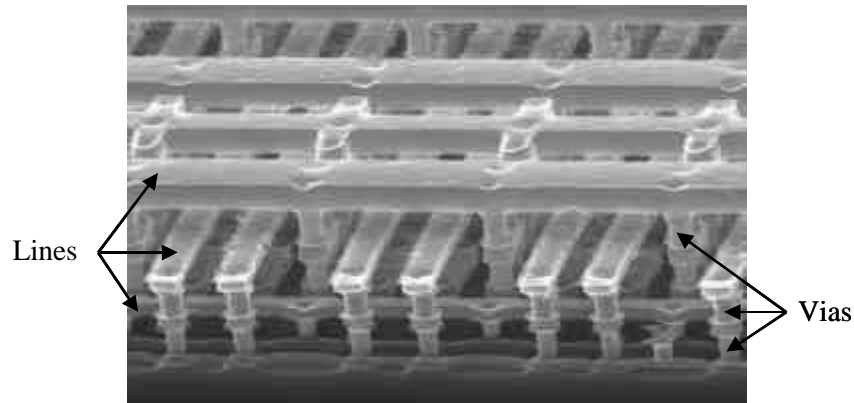
### ***Clean Room Environment***

Process operation in a class 10 clean room implies serious constraints, either for functionality, security, or environment contamination control:

- Full automation of the process ;
- Fire detection and extinguishing system integrated in the machine ;
- Equipment placed on a spill trough to contain condensed water or solvent leak ;
- Machine covered and set in depression, in order to exhaust a potential gas leak or any particle generated by the process elements.

## **II. APPLICATIONS FOR ULK / Cu INTEGRATION**

In integrated circuits, semiconductor components are connected by a web of metallic contacts, either vertical (vias) or horizontal (lines). Figure 4 presents an interconnect structure of 3 levels of vias and lines. For advanced devices, as much as 9 levels of copper interconnections are realized.



**Figure 4:** SEM picture of a metal interconnect structure obtained by selective etching of the dielectric (© CEA-Léti)

Lines and vias are typically 200 nm thick and wide. Metal lines are insulated to each other by a dielectric material. The properties of this material are a compromise between a low dielectric constant, a high mechanical and thermal resistance (it must support a temperature of 450°C during the curing of copper). Most dielectrics in development are nanoporous Methylsilsequioxane-based films, with a dielectric constant between 2.0 and 2.5. These films are deposited by chemical vapour deposition (CVD) or by spin-on of an organic solution. An open porosity is generated in plasma or by thermal cure.

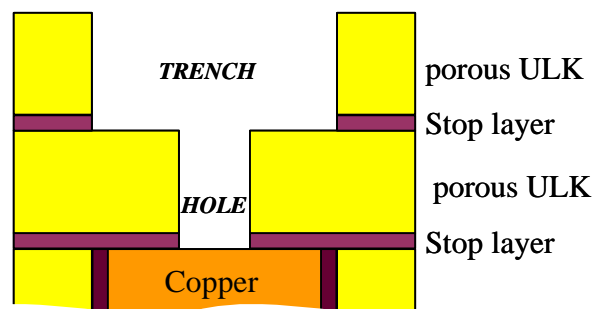
Figure 5 illustrates a generic dual damascene structure, before diffusion barrier and copper deposition. Metallic lines fill trenches and vias fill holes. The main damages of ULK occurring during integration are:

- Poisoning and degradation during plasmas used for etching and stripping ;
- Contamination of sidewalls and bulk of the material by copper during breakthrough of lower stop-layer ;
- Diffusion of the copper diffusion barrier during CVD deposition (typically TiN);
- Deposition of residues on sidewalls during etching (side wall polymers, including copper by-products during the breakthrough of the stop layer) ;
- Poisoning during wet cleans.

Supercritical fluids can be used as complementary treatments to restore the dielectric material, by rinsing and curing deep inside the porosity. But they can also even challenge some of existing processes, like photoresist stripping or wet cleans.

### ***Curing - Depoisoning***

As deposited, a porous SiOCH (JSR LKD 51-09) is hydrophobic, characterized by a contact angle with water of about 105°. Its dielectric constant is 2.2. Oxidizing plasmas used during dielectric etching or photoresist stripping modify the surface of the dielectric by converting



**Figure 5:** conventional dual-damascene structure after stop layer breakthrough in BEOL. Walls of the ULK are particularly exposed to contamination.

Si-CH<sub>3</sub> bonds to Si-OH bonds. This leads to a dramatic reduction of contact angle to a value of 3°. Water contamination and OH bonds are observed by IR absorbance, and the dielectric constant rises from 2.2 to 4.5 – 5.5.

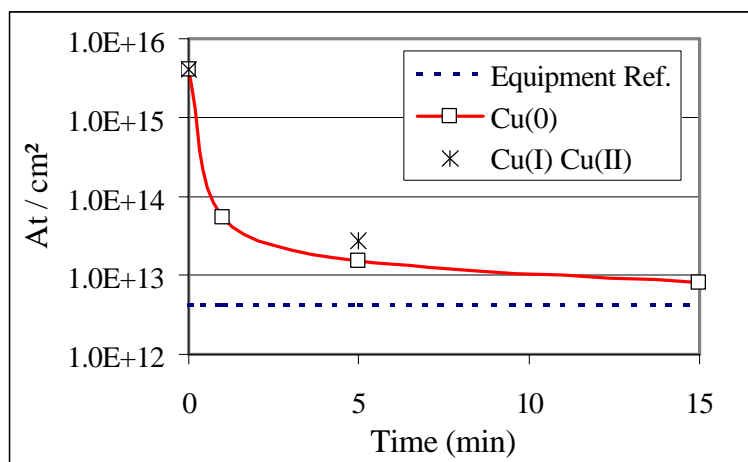
Thermal annealing under vacuum at 425°C during 30 min allows a partial restoration of the dielectric constant at 2.8, because of incomplete and non-permanent water removal. On this dielectric layer, we performed an extraction of water with pure supercritical CO<sub>2</sub> followed by a short impregnation with hexamethyldisilazane (HMDS) at 1% weight concentration in CO<sub>2</sub> at 100°C and 80 bar. HMDS is known to react with -OH end-groups and form -O-Si-(CH<sub>3</sub>)<sub>3</sub> hydrophobic end-groups. Contact angle of the dielectric was restored to 110° and then stable versus time.

Ability of supercritical CO<sub>2</sub> was previously demonstrated to remove organic contaminants from the porous dielectric, and especially amines, responsible for lithography defects in following stages of integration (this is called resist poisoning) [2].

### ***Copper contamination removal***

As explained before, the etching of the Cu stop layer provokes a back sputtering of copper particles on the sidewalls of the ULK. B. Xie & al. demonstrated that copper contamination on a silicon oxide layer can be addressed with hexafluoroacetylacetone (Hfac) dissolved in supercritical CO<sub>2</sub> [3].

In order to evaluate the efficiency of this process on a porous ULK, Cu<sup>(0)</sup> was deposited by CVD on a 300 nm thick layer of porous ULK (JSR LKD 51-09) on Si wafers. VPD-AAS (Vapour Phase Decomposition - Atomic Absorption Spectroscopy) of the wafers showed a contamination of a few 10<sup>15</sup> at/cm<sup>2</sup> of Cu. A part of the wafers were oxidised by UV/O<sub>3</sub> treatment in order to convert Cu<sup>(0)</sup> into CuO and Cu<sub>2</sub>O. Wafers were cleaned on a bench-scale equipment in static conditions at 180 bar and 61°C with 1000 ppm Hfac in an ethanol / CO<sub>2</sub> mixture. Cleaning results are presented on figure 6. The equipment reference is the Cu contamination brought by the bench-scale apparatus on a clean Si wafer. A cleaning efficiency of 99.7 % for Cu<sup>(0)</sup> is obtained in 5 min, confirming results published by B. Xie al.



**Figure 6:** Remaining Cu contamination vs cleaning time by Hfac in SC CO<sub>2</sub>

### ***Photoresist Stripping***

After lithography, remaining resist on the wafer and post-etch residues can be compared to a crust, insoluble in any solvent, and typically removed in two steps by plasma oxidation (called "ashing") and wet cleaning for residues elimination.

Selectivity of such treatments towards SiOC ULK is not sufficient, and new processes are appearing.

Many works deal with supercritical fluids stripping of photoresist [4], [5]. Classical methods to eliminate photoresist by supercritical CO<sub>2</sub> and co-solvents are diffusion, swelling and delaminating of the crust by pressure variations and/or fast decompression. Unfortunately, stripping efficiency by SC CO<sub>2</sub> and co-solvents mixtures presently published, are still lower than plasma ashing, especially for the removal of the residues.

Three solutions are now under investigation:

- Elaborate a chemistry to weaken the crust in supercritical CO<sub>2</sub> ;
- Use additional mechanical effects to increase SC CO<sub>2</sub> –based stripping efficiency (with the risk to deteriorate the ULK layer and the very fine device structures) ;
- Operate a preliminary soft ash of the photoresist by plasma before supercritical CO<sub>2</sub> cleaning.

## CONCLUSION

This prototype will allow developing processes with supercritical CO<sub>2</sub> at pre-industrial scale for the manufacture of silicon wafers. Its efficiency for cleaning and stripping steps will be evaluated and compared to competing processes for the integration of the porous dielectric materials.

## ACKNOWLEDGEMENTS

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