$ScCO_2$-based Processes In Semiconductor Manufacturing: Why Did It Fail ?

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During the first half of this decade, almost everyone involved in semiconductor manufacturing research assumed that some -lab-scale proven- supercritical CO_2-based processes could offer significant improvements over some specific, existing IC processing steps. However, if one tries to implement these processes in bigger (full wafer scale) reactors, and in a high demanding, ultra clean (IC manufacturing compatible) processing environment, a number of serious issues are encountered. Hardware-related problems, as well as process-related problems like lack of reproducibility, uncontrollable background contamination, material compatibility issues, and within-wafer inhomogeneities are the mayor hurdles to be taken in order to be accepted in standard, high volume IC manufacturing. As a result of this, almost every IC- and processing tool manufacturer world-wide, stopped working on developing $scCO_2$–based processes.

INTRODUCTION

Nothing less than a ‘hype’ existed in semiconductor manufacturing research during the first half of this decade. In response to needs for material-compatible cleaning systems, small-dimension developing solvents, and low chemical-use processes, almost everyone assumed that supercritical CO_2-based technologies would offer process applications that are both process enabling and provide potential for chemical abatement in microelectronics engineering. Examples of such process steps included stripping of photo resist and residues, drying after wet cleaning/etching, developing and spinning of resist, chemical fluid deposition of metals, silylation (low-k restoration), and deposition and patterning of low-dielectric materials [1,2].

Indeed, at first sight supercritical CO_2 ($scCO_2$) exhibits a number of interesting & beneficial properties: it diffuses rapidly, has low viscosity, near zero surface tension like a gas, and thus, can penetrate easily into deep trenches and vias. It also enables cleaning and drying of high aspect ration structures without pattern collapse or stiction. $scCO_2$ has the solvating properties of a liquid and thus can dissolve chemicals, such as alcohols and fluorinated hydrocarbons, forming a homogenous supercritical fluid solution. Moreover, CO_2 is relatively cheap, non-toxic and in principle relatively easily recyclable.

It is a fact that most of the above described processes did indeed show promising results using small lab-scale high pressure reactors, in which only small Si substrates (i.e. Si wafer pieces with a size of a few cm^2) were processed. However, if one tries to implement these processes into bigger, full wafer scale reactors (i.e. for Si substrates with diameter of 20 to 30cm), and in an ultra clean (IC manufacturing compatible) processing environment, a number of serious issues have been encountered. In this paper, an overview will be given of some of these issues, encountered at IMEC, a nano-electronics research institute. The main hardware-related problems, as well as process-related problems will be listed and briefly discussed.

RESULTS AND DISCUSSION

1. Process background level of metals

The IC manufacturing environment is extremely demanding in terms of cleanliness of a process step. The maximum allowable level of added metals on the Si surface must be lower than 10^{10} atoms.cm^{-2}. Also, less then 1 added particle (bigger then 22nm) per cm^2 is allowed. It is clear that these requirements are very challenging for $scCO_2$ processing tools. Some data are shown here to illustrate this point.

Figure 1 displays the added iron surface contamination on a full silicon wafer, after treatment with pure $scCO_2$. As can observed, concentration levels are not too dramatic most of the time.

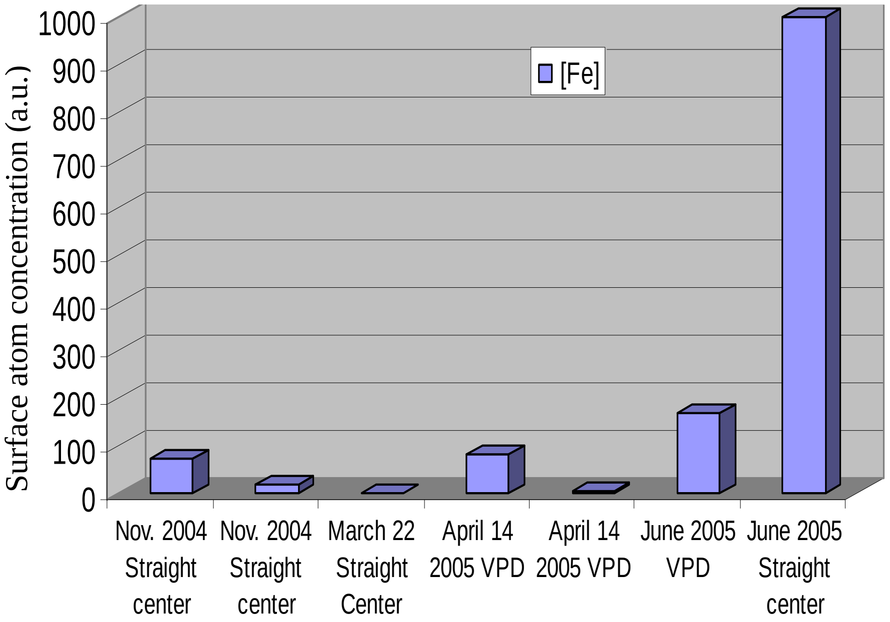


Figure 1 : Added iron contamination on the Si wafer surface after treatment with pure $scCO_2$, measured at different points in time. Concentrations measured with TXRF.

However, the value of the last measurement on the graph (on the right) is extremely high. It turned out that the CO_2 used at this point came from a newly hooked-up cylinder skid, indicating that (i) the metal contamination in this case originates from the CO_2 (and not form the tool hardware), and (ii) the CO_2 itself is contaminated by the corroded inside of the steel CO_2 cylinders, generating nano-sized Fe_2O_3 clusters. These findings were confirmed with other, more specific tests: The liquid CO_2 from the cylinders was expanded though a nozzle into CO_2 ice. This ice was collected onto a clean Si wafer, and was then sublimed under a controlled, clean N_2 environment. The resulting added contamination on the wafer surface confirmed the above findings.

Also, increasing the *total duration* of a $scCO_2$ process, increases the metal concentration on the wafer, independently from the process *flow* variations (i.e. number of pressurization/depressurization cycles) ! Going from a 3’ process to a 12’ process (or 4x3’), increases the Fe concentration on the wafer with about a factor of 4. There is no correlation with the *total* amount of CO_2 used as such.

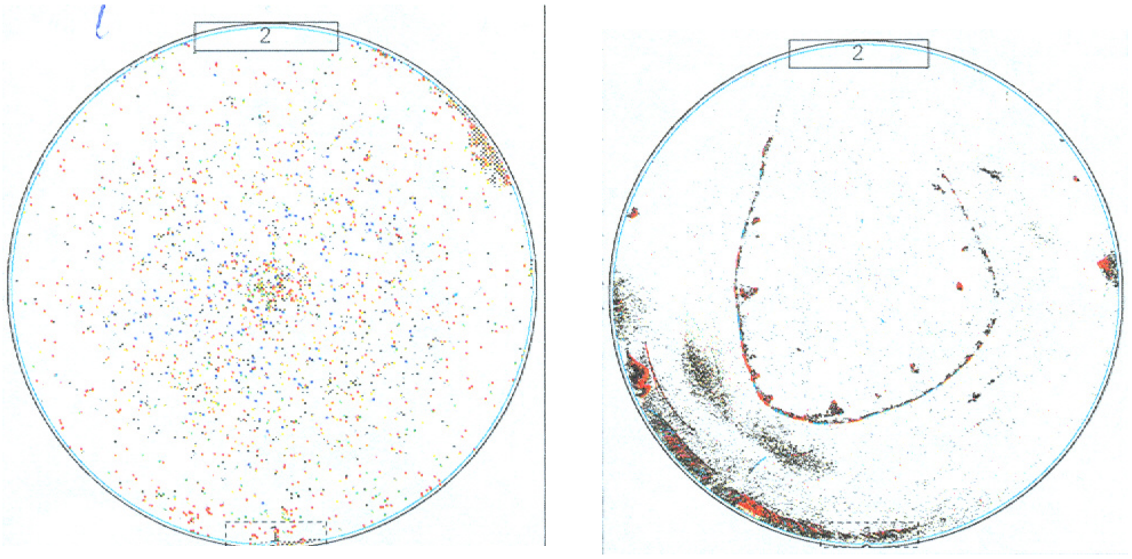
Clearly, a major lesson here is to use only aluminum tanks and cylinders for CO_2 storage.

2. Process background level of particles

In standard IC-processing tools using gases and/or liquids, particle background contamination levels are reasonably well controlled by using efficient and reliable in-line filters and purifiers. However, such filters are not commercially available for dense CO_2. One can use ceramic-based filters, but they can get clogged by additives/co-solvents and have a limited lifetime when exposed to frequent pressurization/depressurization cycles. Moreover, their cut-off region is around 300nm, which is rather high.

Particles originate mainly from the tool hardware (‘dirty’ vessels, tubes and valves), and to a lesser extend from the CO_2 itself. As a general rule, it can be stated that: (i) the number of particle adders does not scale with process time (and thus CO_2 flow), e.g. a 12’ process performs as well as a 3’ process; (ii) the number of particles on a wafer scales with the number of fast pressurization/depressurization cycles it has seen; (iii) processes using low flows and/or constant pressure conditions do not generate significant amount of particle adders; (iv) there is no correlation between the levels of particle background contamination and metal background contamination.

Particle performance does depend on: substrate type, CO_2 phase (liquid or supercritical), type of additive/cosolvent, … This is illustrated in the following figure, where wafer particle maps of hydrophilic wafers are displayed after 2 different treatments of pure dense CO_2. Clearly, the supercritical CO_2 process performs the best.



(a) (b)

Figure 2 : Wafer particle map of a hydrophilic wafer after (a) supercritical CO_2 treatment, and (b) liquid CO_2 treatment. Particles are detected as light point defects using a light scattering detection tool (KLA-SP1, 0.1-0.3µm bin size)

Remarkably, the opposite behavior is observed for hydrophobic wafer surfaces, as can be seen in figure 3.

The particle background level of a process depends on a multitude of conditions, and is probably one of the most difficult issues to solve/control. The behavior of particles in lowpolar solvents in general is yet not well understood and is an area of increasing interest and research. Clearly, a recommendation to reduce the particle background level is to start with a tool of which the complete inner surface, which comes into contact with dense CO_2, is as clean as possible. For high pressure tool parts like valves, connectors, pressure- and flow-regulators etc., this is very often not a trivial thing to realise. Also, all the chemical additives and co-solvents must be filtered before use.

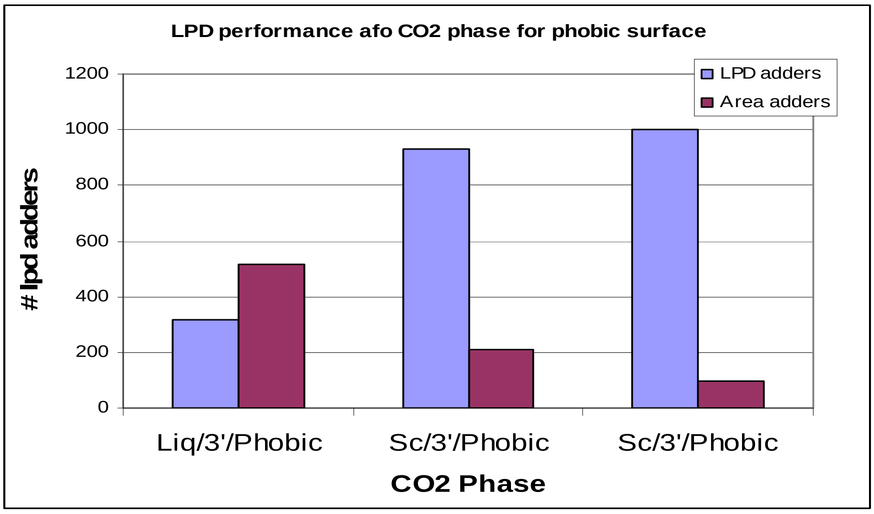


Figure 3: Total particle count on a hydrophobic wafer surface after pure liquid CO_2 treatment (bars on the left side), and supercritical CO_2 treatment (middle and right bars) in non-optimized conditions. Particles are detected as light point defects using a light scattering detection tool (KLA-SP1, 0.1-0.3µm bin size)

3. Within wafer non-uniformity of process

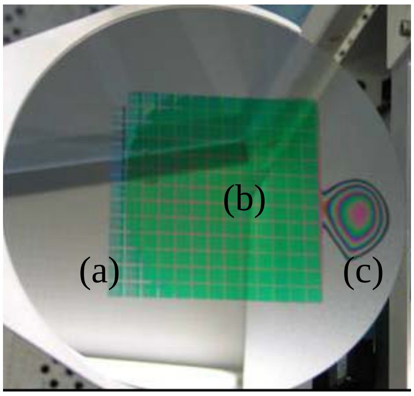


Figure 4: Top surface of a wafer after a $scCO_2$–based photo resist development process. Three different areas are visible: a zone of over-development (a), correct development (b), and under-development (c).

In IC processing, it is required that the applied process acts in a uniform way over the whole wafer surface. This means that pressure, temperature, flow rate, additive concentration, etc. must be as uniform as possible. For some type of processes, this seems to be a difficult condition to meet. An example is given in figure 4, showing a wafer after a photo resist development process in $scCO_2$ + additive, performed in a single-wafer reactor. Clearly, three different zones can be distinguished, indicating non-uniformities in the development process due to peculiarities of the fluid dynamics in the high pressure reactor.

4. Process reproducibility

For some specific process applications, it seems not to be straightforward to reproduce the process results which are described in literature. E.g. in the case of post-etch residue removal for BEOL Cu/low-k structures, we tried to perform this cleaning step using 2 different, successful chemistries/recipes developed by other research groups. To our surprise, none of them worked properly: the first one just did not clean, and the second one did clean, but caused at the same time corrosion to the Cu-lines (which is of course unacceptable).

On the other hand, it is reported by several R&D groups that they cannot always reproduce themselves their own developed $scCO_2$ processes (i.c. deposition processes).

This clearly indicates a lack of understanding of all the parameters controlling the high pressure processes. It is believed that reactor conditioning & cleanliness, and trace contaminations in the CO_2 itself (e.g. moisture content) may play a significant role here.

5. $ScCO_2$ "peculiarities"

Two examples are give here to illustrate problems which can arise in a process due the low solvating power of $scCO_2$.

Figure 5 shows the backside of a wafer after being processed by a $scCO_2$ process using additives. The white concentric rings correspond to the positions of the rings in the wafer chuck in the reactor. These chuck rings are kept at a slightly lower pressure to keep the wafer in a fixed position. However, the resulting lower CO_2 density in these rings caused a decrease of the solvating power and an out-crashing (deposition) of the specific additives used. This is of course unacceptable.

Figure 5: Back side of a wafer after a $scCO_2$–based process using additives. The concentric rings are formed by deposited additives due to a pressure drop in the rings of the wafer chuck.

A second example has also been discussed in another paper of our group presented in this conference. It was found that sacrificial SiO_2 in high-aspect ratio structures can be etched away very efficiently (thus without pattern collapse) using a $scCO_2$ process with the 'HF/Pyridine' adduct as additive. However, the main product of this etching reaction is the $(Pyr)_2SiF_4$ adduct, and is completely insoluble in $scCO_2$. Ironically, this product can only be removed by dissolution in water, thus causing again pattern collapse of the high aspect ratio structures…

6. Hardware requirements

A trivial requirement for a processing tool in order to be accepted in a standard IC manufacturing line, is a throughput of about 2 minutes per wafer. Again, this is a very challenging target for high pressure tools. In the case of a single-wafer reactor, it almost impossible to load a wafer, pressurize, process, rinse, depressurize and unload a wafer in 2 minutes or less. This means that one has to opt for a batch type reactor (20 wafers per process cycle), or for several single wafer reactors in parallel operation. In both cases, the tool investment cost and CO_2 consumption will become unacceptably high.

Another requirement is that the tool downtime must be lower than 10%. Ideally, tools must operate 24hrs a day and 7 days a week. The frequent pressurization/depressurization cycles and valve operations are very demanding for the high pressure seals in several parts of the tool, resulting in frequent leakages and/or blocking of valves. The design and material choice of sealing rings is clearly immature and must be improved significantly in order to achieve a required performance.

Another thing to take into account is the cleanability of valves, flow controllers and pressure relieve valves. Chemical additive tend to stick into dead spaces and on/in sealing rings. After some time these tool parts become a (particle) contamination source of their own.

CONCLUSION

As partially illustrated by the examples given above, the reasons why $scCO_2$-based processes were not successful to be introduced in standard IC-manufacturing are three-fold: (1) The state-of-the-art hardware is immature in terms of reliability, uptime and background contamination control. (2) Lack of understanding of process non-reproducibility and non-uniformities (fluid dynamics). (3) And last but not least: the absence of real ‘killer applications’. As long as this last condition is not met, $scCO_2$ based processes will not be in used IC-manufacturing.

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