

## Removal of photoresist by O<sub>3</sub>/DI-water processes: determination of degradation products

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### INTRODUCTION

For the removal of organic contamination including photoresist (PR) and residues thereof, processes based on aqueous ozone chemistry are extensively used since a few years<sup>[1]</sup>. These environmentally benign processes combine an effective cleaning with a lower cost of ownership.

In general the oxidation mechanisms of organic material by ozone / DI mixtures are very complex. The same parameters influence both the physico-chemistry of ozone in water as well as the kinetics of the reactions between ozone and the organics<sup>[2]</sup>.

Furthermore, the typical throughput driven short process times don't allow a complete degradation of all organics and PR into CO<sub>2</sub> and water as is often assumed. Low molecular weight oxygen containing and typically good soluble fragments do remain in the aqueous solution<sup>[3]</sup>. These compounds show a very low reactivity towards ozone. Because DI water is the most used "chemical" in the micro-electronic industry, re-use and/or regeneration becomes a very important issue. Both identification and quantification of the organic loading of the process water will allow efficient regeneration thereof.

### EXPERIMENTAL

In this study the degradation products of ozone reactions with two types of commonly used photoresists (I-line and DUV resist) are determined by means of Ion Chromatography (IC) and headspace GC-MS (HS GC-MS). Also the behaviour of these degradation products during further ozonation and their stability in water were investigated<sup>[4]</sup>. Experiments with both I-line and DUV resist were performed in a spray processing tool with reclaim capabilities. At first, a tool blank was taken from the reclaim tank. A first, second and third sample were taken after respectively stripping one, two and three full batches of PR coated wafers. After stagnation of the process water in the tank (sample 4) for approximately 14 hours, two blank ozone treatments with no input of new PR material, were carried out (sample 5 and 6). Considering the stability in water of these compounds IC and HS GC-MS were repeated after approximately one, two, five and ten days. Finally, the identification of these low molecular weight oxidation products is interpreted in terms of possible reaction mechanisms.

### RESULTS AND DISCUSSION

Both IC and HS GC-MS measurements showed that carboxylic acids were the most abundant degradation products present in the process water.

In Figure 1 the concentration evolution of the determined carboxylic acids (Acet = Acetic acid, Form = Formic acid, Pyr = Pyruvic acid, Glyo = Glyoxilic acid, Oxal = Oxalic

sampling conditions is given for experiments with the IX845 PR (I-line).

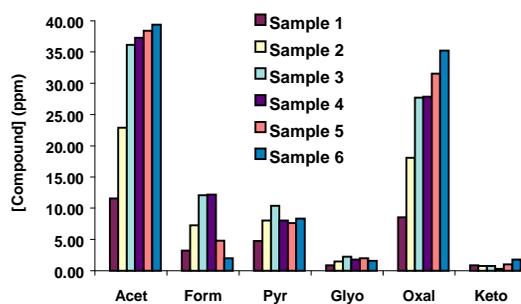


Figure 1: Concentration evolution of determined carboxylic acids as a function of sampling conditions

The concentrations of these compounds increase with the number of processed batches. In addition, most of these degradation products are also very stable towards further ozonation. For the experiments with the DUV resist similar results were obtained: the same carboxylic acids were also the most important degradation products except for the absence of pyruvic acid. Results concerning the stability in water, are given in Figure 2 for the I-line experiments. As is seen, most of the degradation products are very stable products in water.

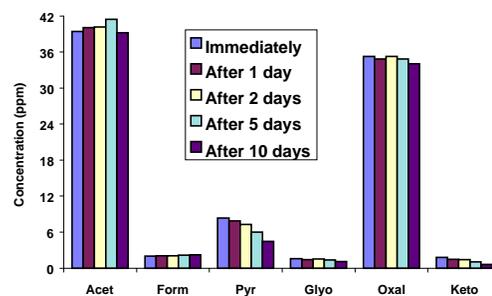


Figure 2: Stability of the determined carboxylic acids in process water

The experimental results were compared with some theoretical predictions based on the chemical structures of the PR's and the reaction mechanisms with ozone. Qualitatively these results were in perfect agreement, e.g. the absence of pyruvic acid in the process waters can be explained by differences in the chemical structures of the PR's.

### CONCLUSIONS

In the removal processes of PR material by O<sub>3</sub>/DI carboxylic acids are the most important degradation products which remain in the process waters. These compounds are very stable in water and have a very low reactivity towards further ozonation. The nature of these degradation products can be theoretically predicted.

### REFERENCES

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acid and Keto = Ketomalonic acid) as a function of