

The removal of organic contamination by O₃/DI-water processes: a theoretical study.

F. De Smedt, H. Vankerckhoven, C. Vinckier, S. De Gendt¹, M. Claes¹ and M.M. Heyns¹

Department of Chemistry KU Leuven, Celestijnenlaan 200 F, B-3001 Heverlee, Belgium

¹ IMEC, Kapeldreef 75, B-3001 Heverlee, Belgium

INTRODUCTION

The use of ozone in wet and dry cleaning processes of silicon wafer surfaces is a fact these days. In the wet processes, ozonated solutions are used for the removal of organic contamination^[1], resist strip^[2] and the oxidation of silicon surfaces^[3,4]. Fundamental knowledge on the reaction mechanisms of the removal of organic contamination is needed in order to improve the cleaning processes. In general, the organic contamination can be divided into 2 classes: saturated and unsaturated compounds. For each type a specific reaction pathway is applicable, namely a radical pathway for the saturated organic species (indirect oxidation) and an O₃-based pathway for the unsaturated species (direct oxidation): Figure 1. Radical species are intermediates formed in the O₃ decay processes.

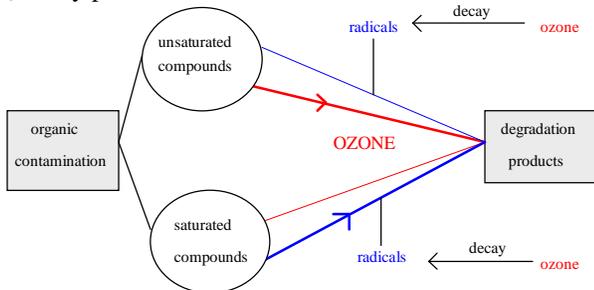


Figure 1: Representation of the reaction pathways for the removal of organics.

OBJECTIVES

In an experimental study, the decomposition of O₃ was characterised as a function of pH, temperature and nature of the additives^[5]. To correlate these experimental results with the build-up of radical species, the O₃ decay has to be modeled. The two models often cited are the HEA- and the TFG-model^[6]. Based on these models, the O₃ decay will be simulated with the Facsimile software^[7]. By this approach it is possible to gain insight in the radical pathways. This information is vital for further improvement of the silicon surface cleaning processes.

RESULTS AND DISCUSSION

During O₃ decay, the following radicals are considered: HO₂, HO₃, HO₄, O₂⁻, O₃⁻ and OH. These radical species are highly reactive, even with saturated C-C bonds.

In order to evaluate the effect of pH and [O₃]₀ on the presence of these radical species in the solution, a 'Radical Pool' is defined as the sum of the concentration of all radicals (RP = ∑[rad]_i). This 'Radical Pool' is clearly dependent on pH: Figure 2. At low pH not only the ozone decay is slow^[5], but also the RP-value is very low (Fig. 2). From pH 4-5 on, a (fast) increase in the RP is observed.

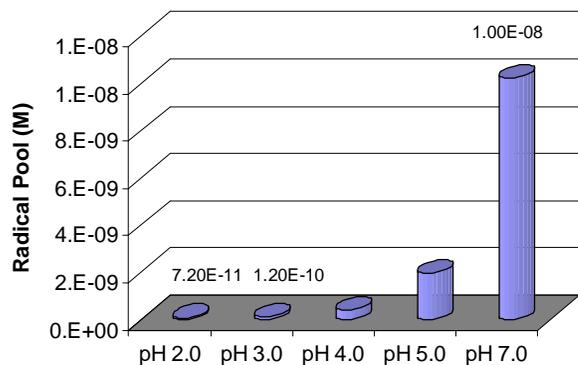


Figure 2: RP (expressed in mol/l) as a function of pH (HEA-model at RT; [O₃]₀ = 10⁻³ M = [O₂]₀)

The dependence of the RP on [O₃]₀ is also different for acidic and alkaline pH. In the former case, no dependence of the RP on [O₃]₀ is observed whereas at pH 9, the RP is positively correlated with the initial O₃ concentration. It is clear that for achieving the radical pathway, one needs to work at near-neutral to alkaline pH-values.

Which is now the most dominant radical species in the solution at acidic and alkaline pH? This depends strongly on the pH as shown in Table 1. The most abundant species at low pH is HO₂ and O₃⁻ at an alkaline pH (of 9).

Table 1: Relative contribution to RP of the radical species (%) at pH 2 and 9 (RT; HEA-model).

	pH 2.0	pH 9.0
HO ₂	89.8	1.6
HO ₃	2.0	2.3
HO ₄	7.9	8.8
O ₂ ⁻	0.10	1.0
O ₃ ⁻	4 10 ⁻⁴	85.4
OH	0.11	0.8

One sees that not only RP increases with pH, but also its relative composition. Correlations between the O₃ cleaning and oxidizing efficiency with RP will further be checked.

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