



Master's Thesis of Engineering

# Formation of hydrogen peroxide by the VUV/UV process: Affecting factors and CFD modeling

VUV/UV 공정 내 과산화수소 발생에 대한 연구

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## Abstract

## Formation of hydrogen peroxide by the VUV/UV process: Affecting factors and CFD modeling

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Recently, as the size of the electronic industry increases, the demand for ultrapure water (UPW) in the semiconductor industry is increasing. Raw water goes through various water treatment processes such as reverse osmosis, ultra-filtration, and UV oxidation to satisfy the quality of UPW. In the UV oxidation process, VUV/UV lamp emits 185 nm and 254 nm wavelengths light simultaneously and is used to remove dissolved organic carbon. At 185 nm, water decomposes to various radicals which generate hydrogen peroxide ( $H_2O_2$ ). When  $H_2O_2$  remains in UPW, the semiconductor wafer can be oxidized which results to low quality product. Many previous studies have tried to identify  $H_2O_2$  formation mechanism, but the exact conclusion has not yet been concluded. In this study, a multiphysics simulation of VUV/UV photoreaction including computational fluid dynamic (CFD) used for analyzing  $H_2O_2$  formation mechanism. According to the simulation results, when dissolved oxygen (DO) exists  $H_2O_2$  was generated through both 'OH self-recombination reaction and  $HO_2$ ' and  $O_2$ ' combination reaction, and  $HO_2'/O_2$ ' disproportionation was the reason of pH difference on  $H_2O_2$  formation. In the absence of DO,  $H_2O_2$  was not produced, there was a correlation between DO and  $H_2O_2$  formation, which suggested that the reaction of oxygen (O<sub>2</sub>) and H' is the most important one on  $H_2O_2$ formation in UV oxidation process.  $H_2O_2$  formation increases when organic matter exists supported the formation of  $H_2O_2$  through  $HO_2$ ' and  $O_2$ ' combination reaction.

**Keyword:** Multiphysics simulation, Hydrogen peroxide, pH, Organic matter, Dissolved oxygen, OH radical steady state concentration

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## **Chapter 1. Introduction**

Ultrapure water (UPW) is highly purified water that eliminates contaminants such as microorganisms, ions, organic and inorganic compounds to extremely low levels (Lee et al., 2016). Global water intelligence (GWI) has reported that by the end of 2025, UPW market will be over \$4000 million, (Lee et al., 2016) and UPW usage in semiconductor manufacturing processes will increase (Kwon et al., 2020). UPW demanding purity quality level varies depending on the industry used, and semiconductor industry requires the highest purity. During semiconductor manufacturing process, UPW is used for rinsing and cleaning chemicals and contaminants on the surface of wafers before and after each process. UPW is manufactured through various processes, which can be classified into three stages: pretreatment stage, primary deionization water, and polishing loop (Kwon et al., 2020; Lee et al., 2016; Zhang et al., 2021). At the pretreatment step, most of the particles and dissolved organic matters from raw water are effectively removed by ultra-filtration and reverse osmosis, but low molecular weight compounds such as methanol, iso-propyl alcohol (IPA), and urea are difficult to remove to the target water quality (Choi and Chung, 2019b; Choi et al., 2016).

To eliminate residual organic compounds, the ultraviolet (UV) oxidation process is used at the end of the reverse osmosis process because if trace amounts of contaminants remain in UPW, the quality and productivity of the semiconductor will deteriorate (Choi and Chung, 2019a; Jin et al., 2018; Kwon et al., 2020; Libman et al., 2015). In the UV oxidation process, vacuum UV/UV (VUV/UV) lamp is used to effectively remove residual organic compounds which emits light of 185 nm (VUV) and 254 nm (UV-C) wavelengths simultaneously (Gonzalez et al., 2004; Zoschke et al., 2014). The two wavelengths' roles are different, the UV-C photon is mostly used for direct disinfection, and the VUV photon (absorption coefficient at 185 nm =  $1.8 \text{cm}^{-1}$ ) generates a powerful non-selective oxidant hydroxyl radical ('OH) which can remove residual contaminants (eqs (1) and (2)) (Weeks et al., 1963; Zhang et al., 2020). According to the previous studies, reactive species ('OH, hydrogen atom (H'), and hydrated electron (e<sup>-</sup><sub>aq</sub>)) generated by water homolysis create H<sub>2</sub>O<sub>2</sub> through radical propagation and termination reaction, and if H<sub>2</sub>O<sub>2</sub> remains in UPW, semiconductor wafers can be oxidized which results to low quality product.

$$H_2 O + h v_{185} \rightarrow {}^{\bullet} O H + H^{\bullet}, \ \Phi_{n1} = 0.33$$
 (1)

$$H_2 O + h v_{185} \rightarrow O H + H^+ + e_{ag}^-, \Phi_{p2} = 0.045$$
 (2)



Figure 1. Example of UPW production process (Kwon et al., 2020)

Many previous studies have tried to identify the  $H_2O_2$  formation mechanism, but exact conclusion has not yet been concluded. During the UV oxidation process, it is difficult to analyze the process precisely because of the short lifetime of radicals (Zhang et al., 2020), and more than 30 reactions react quickly at the same time, it is difficult to know which reaction is the main factor. Previous studies have estimated  $H_2O_2$  formation mechanism indirectly by comparing the results when the experimental condition changed such as solution pH (Nosaka and Nosaka, 2017), organic matter concentration (Azrague et al., 2005; Imoberdorf and Mohseni, 2011; Robl et al., 2012), and dissolved oxygen (DO) existence (Du et al., 2021; Robl et al., 2012; Yang et al., 2018; Zhang et al., 2020). At this time, different results and discussions were proposed for the same variables, because results were indirectly inferred through known reaction equations due to the difficulty of accurate analyzing the reactions in the reactor.

Recently, multiphysics simulation including computational fluid dynamics (CFD) have been presented as an effective tool for interpreting complex processes in the reactor. Reason that difficult to prove the mechanism is because the reactions inside the reactor can't be directly analyzed. However, simulation can analyze the changes inside the reactor by simultaneously calculating the fluid dynamics governing equations and the chemical and photolytic reactions. Bagheri and Mohseni used multiphysics simulation to analyze the UV oxidation process, but the research team used simulation to predict pollutants degradation and analyze the decomposition factors according to the reactor condition changes (Bagheri and Mohseni, 2014; Bagheri and Mohseni, 2015).

The objective of the present study was to develop the UV oxidation process model with the multiphysics software and analyze how  $H_2O_2$  generated precisely during the oxidation process. To validate the simulation data, experiments were conducted using lab-scale fluidic annular photoreactor, by changing experimental conditions. Three variables (solution's initial pH, DO and organic matter concentration) were selected for the model development and to analyze  $H_2O_2$  formation mechanism. These results provided the mechanism of  $H_2O_2$  generation during the UV oxidation through quantitative evidence and suggest that developing a multiphysics simulation model could use for in-depth chemical mechanism analysis which occurring in the reactor.

## **Chapter 2. Materials and Methods**

#### 2.1. Reagents

All chemicals were used of reagent grade and used without further purification. Chemicals used in this study include caffeine, iso-propylalcohol (IPA), methanol, urea, p-hydroxyphenylacetic acid and horseradish peroxidase all were obtained from Sigma-Aldrich and perchloric acid was obtained from Dae Jung. High purity gases, nitrogen (N<sub>2</sub>) and air gas (N<sub>2</sub> 79%, O<sub>2</sub> 21%) were used for controlling the DO concentration. All solutions were prepared using deionized (DI) water (>18.2 M $\Omega$ cm, Millipore, Burlington, MA, U.S.A.).

#### **2.2.** Experimental setup and procedure

Figure 2. schematically shows the structure of the flow type VUV/UV reactor used in this study. Irradiation was conducted using the 373 mL annular shape SUS 304 VUV/UV reactor, total length of 320 mm with a diameter of 45 mm, contained a 290 mm long single 42 W low-pressure mercury amalgam ozone-generating lamp (GPHA357T5VH, UV Nature), with a diameter of 15 mm, installed axially, surrounded by the synthetic quartz sleeve (UV Nature). The synthetic quartz sleeve was 80% transparent to VUV irradiation. The inner diameter of quartz sleeve was 20.5 mm and the outer diameter of quartz sleeve was 23 mm. The length of this quartz sleeve vessel was same as the SUS 304 VUV/UV reactor. Input flow of the stock solution was continuously injected in the influent line of the VUV/UV reactor using a gear pump (WT3000-1JA, Longer Pump). The flow rate was 373.0, 497.5, or 746.0 ml/min and their hydraulic retention times were 30, 45, and 60 seconds, respectively. The solution pH was adjusted by using perchloric acid because anion of this acid does not participate in the reactions (Sehested et al., 1968). DO concentration in the feed flow was controlled by purging nitrogen gas (N<sub>2</sub>) and air gas before the radiation. The absolute emission power of the lamp was determined by UV spectrometer (OHSP350UVS, Hopoolight). In order to determine the extent of 'OH steady state concentration (['OH]<sub>ss</sub>) production, caffeine was selected as probe compound due to its UV-resistant (Sun et al., 2016) and was spiked in low concentrations (10  $\mu$ M) inside the stock solution at the beginning of the VUV/UV process.



Figure 2. Schematic description of the VUV/UV photoreaction system.

#### 2.3. Analytical Methods

#### 2.3.1. H<sub>2</sub>O<sub>2</sub> measurement

 $H_2O_2$  concentration was measured using the fluorescence probe method (Chen et al., 2018; L. et al., 1985). Fluorescence reagent was containing 10.8 mg of p-hydroxyphenylacetic acid and 4 mg of horseradish peroxidase in 10 ml potassium hydrogen phthalate buffer solution. The fluorescence data was obtained by fluorescence spectrophotometry (Hitachi F-4500). For analysis, excitation was performed at 315 nm, while monitoring the emission at spectra from 350 to 500 nm.

#### 2.3.2. Caffeine and steady state 'OH concentration measurement

The caffeine concentration was measured by rapid separation liquid chromatography (RSLC) using an UltiMate 3000 HPLC system through Acclaim 120 C18 column for separation (from Thermo Fisher Scientific). From the concentration change of caffeine, the ['OH]<sub>ss</sub> value during the VUV/UV process can be calculated using the following Eq. (3),  $k_{\cdot OH,CAF}$  is the second-order rate constant between 'OH and caffeine at 2.6×10<sup>9</sup> M<sup>-1</sup> s<sup>-1 24, 25</sup>.

$$\int_{0}^{t} [{}^{\bullet}OH] dt = \frac{\ln([CAF]_{0}/[CAF]_{t})}{k_{\bullet OH,CAF}}$$
$$\ln([caffeine]_{0}/[caffeine]_{t}) = \int_{0}^{t} [{}^{\bullet}OH] dt * k_{\bullet OH,caffeine}$$
(3)

### 2.4. CFD Numerical Simulation Methods

#### 2.4.1. Geometrical models and mesh structure

A multiphysics model was developed based on experimental results to simulate the chemical kinetics inside the VUV/UV reactor. For reducing the computation cost, the radial symmetry reactor was considered as an axisymmetric two-dimensional geometry and only half of the geometry was used for simulation. A boundary-layer mesh was setup on the walls, and the two-dimensional simulation domain was discretized with 64000 rectangular mapped meshes quad mapped meshes (Figure 3.).



Figure 3. Detailed view of the the VUV/UV reactor's CFD mesh

#### 2.4.2. Numerical solution method and strategy

Four physics modules in COMSOL Multiphysics software (version 6.0, COMSOL, Inc., Burlington, MA, USA) were incorporated for the numerical simulation: the laminar flow module (spf) for the flow channel, radiation in participating media module (rpm) for the VUV/UV lamp, transport of diluted species (TDS) for the mass transport of chemical species and chemistry (chem) for computing chemical reactions in the reactor.<sup>26-28</sup> The simulation process was performed in two steps. At the initial step, the equations of the laminar flow module and the radiation in participating media module were calculated. Note that the velocity field, pressure field, and incident radiation were assumed to remain constant. With the inlet, the fluid was assumed as Newtonian and incompressible. A stationary flow field (velocity field u and pressure p) was calculated solving laminar flow equations for momentum conservation (Eq. (4)) and continuity equation (Eq. (5)) for mass conservation with the equation (Eq. (6)),  $\rho$  is the density of the solution,  $\mu$  is the dynamic viscosity, F is the volume force vector. and isothermal.

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot [-pI + K] + \mathbf{F}$$
(4)

$$\rho \nabla \cdot (\mathbf{u}) = 0 \tag{5}$$

$$K = \mu(\nabla u + (\nabla u)^T) \tag{6}$$

Flow rate (ml/min)	Hydraulic Retention time (sec)	Reynolds number
746 ml/min	30	311
497.5 ml/min	45	207
373 ml/min	60	155

Table 1. Reynolds number of each process

Simultaneously, the spectral irradiance (G) was calculated from the following (eqs. (7) and (8)) of the P1 approximation method, because P1 approximation gave a realistic radiation profile in an optically thick reaction medium (Cuevas et al., 2007; Leblebici et al., 2017).  $D_{P1}$  is the P1 diffusion coefficient,  $\kappa$  is the absorption coefficient, and  $I_b$  is the blackbody radiative intensity.

$$\nabla \cdot (D_{P_1} \nabla G) - \kappa (G - 4\pi l_b) = 0 \tag{7}$$

$$D_{P1} = \frac{1}{3\kappa + \sigma_s(3 - a_1)}$$
(8)

In the subsequent step, the equations of the transport of diluted species module and the chemistry module were calculated. The mass balance equation for the chemical species *i* is given as Eq. (9):  $D_i$  is the diffusion coefficient of *i*,  $c_i$  is the concentration of *i*, and u is the flow velocity vector obtained from the CFD calculation of the first step.  $R_i$  is the source term from the photolysis reaction calculated using the chemistry module.

$$\nabla \cdot (-D_i \nabla c_i + uc_i) = R_i \tag{9}$$

#### 2.4.3. Boundary conditions

Multiphysics simulation details including initial conditions, boundary conditions, and simulation parameters are arranged. To improve understanding, visualized simulation domains and boundaries of the VUV/UV reactor are shown in Figure 4. Table 2. summarizes the initial and boundary conditions applied in the VUV/UV simulation.



**Figure 4.** Visualization of simulation domain and boundary of the VUV/UV reactor. The corresponding part is shown in purple: (a) flow path domain  $(\Omega_{fp})$  is the domain for the CFD and transport simulation. (b) pipe wall  $(\Omega_{pw})$ , (c) inlet 1  $(\Omega_i)$ , and (d) outlet  $(\Omega_o)$ , are the boundaries for the CFD and transport simulation. (e) participating medium  $(\Omega_{pm})$  is the domain for the radiation simulation. (f) opaque surface  $(\Omega_{os})$ , and (g) lamp  $(\Omega_l)$  are the boundaries for the radiation simulation.

Table 2. Initial and boundary conditions for multiphysics simulations

Equations	Location
$u_x = 0, \ u_y = 0, \ p = 0$	$\Omega_{\mathrm{fp}}$
$\mathbf{c} = \mathbf{c}_{0,i}$	$\Omega_{\mathrm{fp}}$
$GG_i$ (The blackbody radiative intensity at initial temperature)	$\Omega_{ m pm}$

#### **Initial conditions**

#### **Boundary conditions**

Equations	Location
u = 0 (No slip)	$\Omega_{ m pw}$
$u = -U_0 n$ , $c_i = c_{0,i}$ (Normal inflow velocity)	$\Omega_{i}$
$[-pI+K]n = -p_0^{\wedge}n, \ p_0^{\wedge} \le p_0, \qquad \mathbf{n} \cdot D_i \nabla \mathbf{c}_i = 0$	$\Omega_{ m o}$
$-n \cdot (-D_{P_1} \nabla G) = -q_{r,net}, \ q_{r,net} = \frac{1}{2} (4\pi I_{b,w} - G)$	$\Omega_{os}$
$I_i = I_{\text{wall}}$	$\Omega_{l}$

#### 2.4.4. Kinetic modeling

The chemical and photochemical reactions of the VUV/UV process included in the numerical simulation are summarized in Table 3 (Basfar et al., 2005; Bielski et al., 1985; Buxton et al., 1988; Gonzalez et al., 2004; Sonntag et al., 1997). The reactants and products are hypothetical and rate constants are estimated for this study. Note that the rate of photochemical reaction was governed by eq. (10), which interconnected radiation in the participating media module and chemistry module.

$$r_{VUV/UV} = \phi \frac{G}{U_{185/254}} \varepsilon_{H_20} c_{H_20}$$
(10)

where  $\phi$  is the quantum yield, *G* is the incident radiation, U<sub>185/254</sub> is the molar photon energy at each wavelength (185 nm = 6.47 kJ/Ein, 254 nm = 4.72 kJ/Ein),  $\varepsilon_{H_2O}$  is the molar absorption coefficient (0.032 M<sup>-1</sup> cm<sup>-1</sup>), and  $c_{H_2O}$  is the concentration of H<sub>2</sub>O in the specific part of simulation domain (Furatian, 2017; Oppenlander, 2003; Zoschke et al., 2014).

The numerical calculation was based on the finite element method (FEM) using a 64-core processor workstation (AMD Ryzen Threadripper PRO 5995 WX CPU 2.70 GHz, 512 GB memory). A segregated solver was utilized in the flow, radiation, mass transfer, and mass transport problem.

Table 3. List of the reactions us	ed for multiphyscis simulation
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No	Reaction	Kinetic constant	Reference
1	$\mathrm{H_{2}O} + hv_{\mathrm{185nm}} \! \rightarrow \mathbf{\dot{O}H} + \mathrm{H^{\bullet}}$	$\Phi_1 = 0.33 \text{ mol ein}^{-1}$	Gonzalez et al, 2004
2	$H_2O + hv_{185nm} \rightarrow H^+ + e^{aq} + {}^\bullet OH$	$\Phi_2=0.045\ mol\ ein^{-1}$	Gonzalez et al, 2004
3	$\mathrm{H_{2}O_{2}} + hv_{\mathrm{185nm}} \! \rightarrow \! 2^{\bullet}\!\mathrm{OH}$	$\Phi_3 = 0.5 \text{ mol ein}^{-1}$	Gonzalez et al, 2004
4	$\mathrm{H_{2}O_{2}} + hv_{\mathrm{254nm}} \rightarrow 2^{\bullet}\mathrm{OH}$	$\Phi_4 = 0.5 \text{ mol ein}^{-1}$	Gonzalez et al, 2004
5	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	pKa = 11.6	Gonzalez et al, 2004
6	$\cdot OH \rightleftharpoons H^+ + O^-$	pKa = 11.9	Gonzalez et al, 2004
7	$HO_2$ $\rightleftharpoons$ $H^+ + O_2$	pKa = 4.8	Bielski et al,1985
8	$H^{\bullet} \rightleftharpoons H^{+} + e^{-}$	pKa = 9.7	Gonzalez et al, 2004
9	$H_2O \rightleftharpoons H + OH^-$	$K_{\rm W} = 10^{-14}$	Gonzalez et al, 2004
10	$2 {}^{\bullet} OH \rightarrow H_2 O_2$	$k_{10}=5\times 10^9M^{1}\text{s}^{1}$	Gonzalez et al, 2004
11	$HO_2 \cdot + O_2 \cdot \rightarrow H_2O_2 + O_2 + OH^-$	$k_{11}=9.4\times 10^7M^{1}s^{1}$	Bielski et al,1985
12	$2HO_2 \stackrel{\bullet}{\cdot} \rightarrow H_2O_2 + O_2$	$k_{12} = 9.0 \times 10^5  M^{1}  s^{1}$	Bielski et al,1985
13	$\mathrm{HO}_2{}^{\scriptscriptstyle\bullet} + \mathrm{H}^{\scriptscriptstyle\bullet} \to \mathrm{H}_2\mathrm{O}_2$	$k_{13} = 1.0 \times 10^{10}  M^{1}  s^{1}$	Basfar et al, 2005
14	$2e^{-}+2H_{2}O\rightarrow 2OH^{-}+H_{2}$	$k_{14} = 5.5 \times 10^9  M^{1}  s^{1}$	Buxton et al, 1988
15	$e^- + {}^{\bullet}OH \rightarrow OH^-$	$k_{15}=3.0\times 10^{10}M^{\!-\!1}s^{\!-\!1}$	Buxton et al, 1988
16	$e^{-} + O_2 \rightarrow O_2^{-}$	$k_{16}=1.9\times 10^{10}M^{1}s^{1}$	Buxton et al, 1988
17	$e^- + H_2O_2 \rightarrow {}^{\bullet}OH + OH^-$	$k_{17} = 1.1 \times 10^{10}  M^{1}  s^{1}$	Basfar et al, 2005
18	$e^{\text{-}} + H^{\text{+}} \longrightarrow H^{\text{+}}$	$k_{18} = 2.3 \times 10^{10}  M^{\text{1}}  s^{\text{1}}$	Buxton et al, 1988
19	$e^{-} + H_2 O \rightarrow OH^{-} + H^{\bullet}$	$k_{19} = 19 \text{ s}^{-1}$	Basfar et al, 2005
20	${}^{\bullet}OH + H{}^{\bullet} \longrightarrow H_2O$	$k_{20} = 1.0 \times 10^{10}  M^{1}  s^{1}$	Buxton et al, 1988
21	$\mathbf{\dot{O}H} + \mathrm{H_2O_2} \rightarrow \mathrm{HO_2}\mathbf{\dot{+}} + \mathrm{H_2O}$	$k_{21}=2.7\times 10^7M^{1}s^{1}$	Buxton et al, 1988
22	$\cdot OH + O_2 \cdot - \rightarrow OH^- + O_2$	$k_{22} = 2.7 \times 10^9  M^{1}  \text{s}^{1}$	Buxton et al, 1988
23	$\mathbf{\dot{O}H} + \mathbf{HO_2} \mathbf{\dot{\rightarrow}O_2} + \mathbf{H_2O}$	$k_{23}{=}0.8{\times}10^9M^{{}_{-}{}_{1}}s^{{}_{-}{}_{1}}$	Buxton et al, 1988
24	$\mathrm{H}^{\scriptscriptstyle\bullet} + \mathrm{O}_2 \mathop{\longrightarrow} \mathrm{HO}^{\scriptscriptstyle\bullet}_2$	$k_{24} = 2.1 \times 10^{10}  M^{\text{1}}  s^{\text{1}}$	Buxton et al, 1988
25	$\mathrm{H}^{\bullet} + \mathrm{OH}^{-} \rightarrow \mathrm{H}_{2}\mathrm{O} + \mathrm{e}^{-}$	$k_{25} = 2.5 \times 10^7  M^{1}  s^{1}$	Buxton et al, 1988
26	$H^{\bullet} + H_2O_2 \longrightarrow H_2O + {}^{\bullet}OH$	$k_{26}=9.0\times 10^7M^{1}s^{1}$	Basfar et al, 2005
27	$\mathrm{HO}_{2}\textbf{`}+\mathrm{H}_{2}\mathrm{O}_{2} \rightarrow \textbf{`}\mathrm{OH}+\mathrm{O}_{2}+\mathrm{H}_{2}\mathrm{O}$	$k_{27} = 5.3 \times 10^2  M^{1}  s^{1}$	Gonzalez et al, 2004
28	$O_2 \cdot H_2 O_2 \rightarrow OH + OH \cdot$	$k_{28} = 16  M^{\text{1}}  s^{\text{1}}$	Gonzalez et al, 2004
29	$\text{ClO}_4 - + e^- \rightarrow$	$k_{29} = 10^2  M^{1}  s^{1}$	Buxton et al, 1985
30	$R + OH \rightarrow xR$	$k_{30} = 1.9 \times 10^9  M^{1}  s^{1}$	Buxton et al, 1985
31	$\mathbf{R}^{\bullet} + \mathbf{O}_2 \rightarrow \mathbf{RO}_2^{\bullet*}$	$k_{31}=2\times 10^9M^{1}s^{1}$	Sonntag et al, 1997
32	$\mathrm{RO}_{2}^{\bullet} \rightarrow \mathrm{R}_{\mathrm{ox}} + \mathrm{HO}_{2}^{\bullet}$	$k_{32} = 1 \times 10^9  M^{1}  s^{1}$	Sonntag et al, 1997

The reactants/products are hypothetical and rate constants are estimated for this study.

### **Chapter 3. Results and Discussion**

#### 3.1. Multiphysics model validation

To validate the multiphysics model's accuracy, all experiments values were compared with the simulation values at various hydraulic retention times. The ['OH]<sub>ss</sub> concentration was determined by using 'OH probe. Caffeine was used as an 'OH probe because it is not photodegradable and rarely reacts with HO<sub>2</sub>' and O<sub>2</sub>'' (Leon-Carmona and Galano, 2011). The simulation results showed high accuracy (Figure 5), and the results showed that the hydraulic retention time influenced the amount of H<sub>2</sub>O<sub>2</sub> generation because the amount of light irradiation increased as the retention time increased. However, the retention time did not effect on the ['OH]<sub>ss</sub>, because according to previous studies (Bagheri and Mohseni, 2015), the ['OH]<sub>ss</sub> is affected by the flow pattern, and all three conditions show a similar flow pattern to the laminar flow.



**Figure 5.** (a) Simulated values of chemical species distribution in the reactor depending on the initial DO concentration, simulation condition: hydraulic retention time = 60 sec, the maximum and minimum points of the scale were set equally for the same species, (b) experimental and simulation results of outlet  $H_2O_2$  concentration on various hydraulic retention time, experiment and simulation condition: initial pH = 4, (c) experimental and simulation results of retention time, experiment and simulation condition: initial pH = 4, (c) experimental and simulation condition: initial pH = 4

#### 3.2. Effects of each UV on H<sub>2</sub>O<sub>2</sub> formation and decomposition

VUV/UV lamp emits 185 nm and 254 nm simultaneously, background study was conducted to determine the role of each wavelength, and the results showed that the photodegradation of H<sub>2</sub>O<sub>2</sub> was negligible in this system (Figure 6.). The experiments were conducted under the identical conditions by changing only the quartz sleeve. Synthetic quartz glass was used to check effects of VUV light and natural quartz was used to check the role of UV-C light, because VUV light can only transmit the synthetic quartz (Oppenlander, 2003). When calculate the VUV absolute absorption coefficient, it can be assumed that there will be no H<sub>2</sub>O<sub>2</sub> photodegradation by VUV because most of the VUV photon is absorbed by water (water absolute absorption coefficient = 1.8 cm<sup>-1</sup>, and H<sub>2</sub>O<sub>2</sub> absolute absorption coefficient =  $5.5 \times 10^{-3}$  cm<sup>-1</sup>,  $\varepsilon_{185,H202}$  × highest H<sub>2</sub>O<sub>2</sub> formation yield). To examine photodegradation by 254 nm light,  $H_2O_2$  was spiked inside the stock solution (10  $\mu$ M) at the beginning of the process and the outlet H<sub>2</sub>O<sub>2</sub> was compared with initial stock concentration. There was no difference outlet concentration and initial stock solution, which means that photodegradation by 254 nm is negligible and in the flow type UV oxidation system, only the water homolysis reaction by VUV was found to be the main reaction to be considered.



Figure 6. Inlet and outlet of  $H_2O_2$  concentration when irradiate only UV-C

#### 3.3. Effects of pH on H<sub>2</sub>O<sub>2</sub> formation

Figure 7. presents the experimental and simulation results of the outlet  $H_2O_2$  concentration according to the pH. Experiments were conducted between pH 3 to 6 to check which reaction contributes the most on  $H_2O_2$  formation. Regarding the influence of pH,  $H_2O_2$  increased until pH 4, and then decreased as pH increased, and the simulation results showed the same tendency as the experimental values. Since, it was difficult to identify the reason of this result experimentally, various simulations were conducted to identify this phenomenon.



Figure 7. Experimental and simulation results of outlet  $H_2O_2$  concentration depending on the initial pH, (a) DO = 0.26 mM, and (b) DO = 0 mM

First, we determined which reaction contributed the most among the four  $H_2O_2$  formation reactions (reaction  $10 \sim 13$ ) through simulation (Figure 8). Prior studies have suggested  $H_2O_2$  generation mechanism by comparing  $H_2O_2$  according to the DO concentration, if  $H_2O_2$  was detected in anoxic condition, they suggested that 'OH self-recombination reaction acts as main mechanism (Zhang et al., 2020), and if not,  $HO_2$ ' and  $O_2$ ' combination reaction also contributed to  $H_2O_2$  formation (Du et al., 2021). To check each reaction's contribution, simulation was conducted by changing each reaction's rate constant to double or half and compared with default result (Figure 8). As a result, there was a difference when 'OH self-recombination (reaction 10) and  $HO_2$ ' and  $O_2$ '' (reaction 11) combination rates were changed, and reaction 10 showed a larger discrepancy, which means 'OH self-recombination reaction and  $HO_2$ ' and  $O_2$ '' combination reaction simultaneously participate in  $H_2O_2$  formation, and the contribution of 'OH self-recombination reaction was greater.



**Figure 8**. Simulated concentration values of outlet  $H_2O_2$  by changing each  $H_2O_2$  formation reaction rate for various initial pH (a)  $\cdot OH + \cdot OH$  (reaction 10), (b)  $HO_2 \cdot + O_2 \cdot (reaction 11)$ , (c)  $HO_2 \cdot + HO_2 \cdot (reaction 12)$ , and (d)  $HO_2 \cdot + H \cdot (reaction 13)$ 

Since, OH self-recombination reaction contributed the most on  $H_2O_2$  formation, we assumed that pH dependence of OH concentration would be the main cause of effects of pH on H<sub>2</sub>O<sub>2</sub> formation. As shown in Table 3, 'OH concentration can be affected by 4 reactive species (HO<sub>2</sub><sup>•</sup>, O<sub>2</sub><sup>•</sup>, H<sup>•</sup> and e<sub>aq</sub><sup>-</sup>), and <sup>•</sup>OH termination by HO<sub>2</sub><sup>•</sup> or O<sub>2</sub><sup>•</sup> reactions (reaction 22 and 23) act as the main scavenging reaction because H<sup>•</sup> and  $e_{aq}$  (reaction 20 and 21) were mostly changed to HO<sub>2</sub> or O<sub>2</sub> by reacting with DO. To verify this hypothesis, 'OH concentration and the overall kinetic constants of HO2'/O2 combination reaction and 'OH termination by HO2' or O2' were determined according to pH (Figure 9). As a result of the calculation, it was found that HO2'/O2' combination reaction increases to pH 5 and decreases and 'OH termination by HO<sub>2</sub> or O<sub>2</sub> was increased with increasing pH and OH concentration showed the same tendency with H<sub>2</sub>O<sub>2</sub> concentration. With this, the effect of pH on H<sub>2</sub>O<sub>2</sub> formation can be explained as follows. In the UV oxidation process, HO<sub>2</sub> and  $O_2^{-}$  are formed by the combination of  $O_2$ , H<sup>•</sup> and  $e_{aq}^{-}$  respectively and by HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>-</sup> disproportionation, the ratio of the two species change depending on pH. Under acidic condition, the two species are present in the form of HO<sub>2</sub> and change to O<sub>2</sub>. form as pH increases. Therefore, as pH become neutral, 'OH termination rate increases because 'OH reacts more rapidly with O2' than HO2', the 'OH scavenging effect will be greater with increasing pH, which result to H<sub>2</sub>O<sub>2</sub> formation diminish. Due to these two effects, the concentration of 'OH tends to increase up to pH 4 and then decrease, and  $H_2O_2$  also tends to be the same.



Figure 9. (a) Overall  $HO_2'/O_2' + HO_2'/O_2'$  kinetic constant depending on the various pH, (b) overall 'OH +  $HO_2'/O_2'$  kinetic constant depends on pH, and (c) outlet  $H_2O_2$  and spatial 'OH concentration depend on pH

#### 3.4. Effects of DO on H<sub>2</sub>O<sub>2</sub> formation

To clarify the effect of DO, experiments and simulations were conducted at various DO conditions, and the amount of  $H_2O_2$  and the average concentration of chemical species inside the reactor participating in the  $H_2O_2$  formation were measured through the multiphysics simulation. As shown in Figure 10,  $H_2O_2$  was produced at the oxic condition and not detected at the anoxic condition, furthermore the  $H_2O_2$  formation decreased very slowly to DO 0.025 mM, and then decreased rapidly. The simulation results showed the same tendency with the experiment value. According to the simulation results, average 'OH concentration was not significantly affected by DO, and average H' concentration increased as DO decreased, whereas the  $HO_2$ ' and  $O_2$ <sup>--</sup> showed a sharp decrease at certain concentration. Given that the concentration graph shapes of H' and  $H_2O_2$  depending on DO are opposite to each other, it can demonstrate that the H' is the major reason of the  $H_2O_2$  formation difference depending on the DO concentration.



**Figure 10**. Experimental and simulated values of outlet  $H_2O_2$  concentration and spatial average concentration of the 'OH, H',  $HO_2$ ', and  $O_2$ ' inside the reactor depending on the various initial DO, experiment, and simulation condition: initial pH = 4, and hydraulic retention time = 60 sec

In the VUV/UV process, H' was mostly produced by water homolysis (reaction 1), and reacted with 'OH, O<sub>2</sub>, OH', and H<sub>2</sub>O<sub>2</sub>, in UPW (reaction 20, 24 ~ 26). At this time, H' main scavenger varied depending on DO concentration. At the condition with sufficient DO, since DO exist a lot than other species, and rate constant is very fast, DO acted as the main H' scavenger. On the contrary, if there is not enough DO, considering the reaction rate constant and average concentration in the reactor, H<sub>2</sub>O<sub>2</sub> and 'OH become the main scavenger. We determined the contribution of two scavengers in H<sub>2</sub>O<sub>2</sub> generation through simulation. The contribution was estimated by comparing the simulation results when compute except for each scavenging reactions in anoxic condition, which means that both scavenging reactions greatly contribute on H<sub>2</sub>O<sub>2</sub> formation inhibition (Table 4). Through this simulation, it was found that the reaction of DO and H' is a very important reaction to produce H<sub>2</sub>O<sub>2</sub>.

	Hydraulic retention time (sec)	Compute without reaction 20	Compute without reaction 26	Compute without reaction 20, 26
	30	$7.88 \times 10^{-3}$	$5.25 \times 10^{-2}$	3.01
$H_2O_2$ ( $\mu M$ )	45	$6.29 \times 10^{-3}$	$5.99 \times 10^{-2}$	3.69
	60	$5.41 \times 10^{-3}$	$6.58 \times 10^{-2}$	4.23

#### Table 4. Outlet H<sub>2</sub>O<sub>2</sub> concentration for each simulation condition

#### 3.5. Effects of organic matter concentration on H<sub>2</sub>O<sub>2</sub> formation

To clarify the effect of organic matter concentration on  $H_2O_2$  formation, initial organic matter concentration was changed to 10 and 100 µM. Since previous studies has reported that there was residual IPA, methanol and urea after the RO process in the actual UPW manufacturing process, three compounds were selected as a representative organic matters (Choi and Chung, 2019b; Choi et al., 2016).  $H_2O_2$  was generated more as the concentration of IPA and methanol increased but urea did not affect the system (Figure 11). Increased generation of  $H_2O_2$  by IPA and methanol can be described as follows. The decomposition of IPA and methanol by 'OH generates carbon radical and reacts with DO which result to  $HO_2$ ' generation (Eqs (11) ~ (13)) (Sonntag et al., 1997). At this time, the amount of carbon radicals generated by 'OH was obtained through the fitting process in the simulation ( $x_{methanol} = 0.15$ ,  $x_{ipa} = 0.2$ ). As a result, organic matter reacts with the 'OH and produce an additional  $HO_2$ ', which result increasing the amount of  $H_2O_2$  generation by more  $HO_2$ ' and  $O_2$ <sup>--</sup> combination reaction occur, however, in the case of urea, the reaction rate with 'OH is relatively low, so carbon radicals are not produced, and no additional  $H_2O_2$  was produced.

$$^{\bullet}OH + RH \rightarrow H_2O + ^{\bullet}R \tag{11}$$

$$^{\bullet}R + O_2 \rightarrow RO_2^{\bullet} \tag{12}$$

$$RO_2^{\bullet} \to R + HO_2^{\bullet} \tag{13}$$



Figure 11. Effects of initial organic matter concentration on  $H_2O_2$  formation during the UV oxidation process.

To examine the effect of organic matter in more detail, the concentration of  $H_2O_2$ and the average concentration of chemical species inside the reactor, participating in  $H_2O_2$  formation were measured through the multiphysics simulation in various conditions. As shown in Figure 12,  $H_2O_2$  amount increased as the initial organic concentration matter increased, and the concentration of 'OH decreased with increasing organic matter, and other radicals' concentration did not change significantly. In the UV oxidation system, 'OH can be generated through various reactions, but mostly generated by water homolysis (reaction 1). During the UV oxidation process, 'OH can be scavenged by several species and the main scavenger changes depending on initial organic matter concentration. When there is no organic matter concentration, most 'OH is scavenged by H' which generated by water homolysis. However, when initial organic matter concentration increased, when considering the concentration and reaction rate constant, organic matter acts as 'OH main scavenger. As a result, the concentration of 'OH tends to decrease gradually as the organic matter increases.



**Figure 12.** Experimental and simulated values of outlet  $H_2O_2$  concentration and spatial average concentration of the 'OH, H',  $HO_2$ ', and  $O_2$ ' inside the reactor depending on the various initial organic concentration, experiment and simulation condition: initial pH = 4, and hydraulic retention time = 60 sec

## 4. Conclusion

In this study, experiments and simulations were conducted by varying the initial pH, DO concentration and organic matter initial concentration. Multiphysics simulation was used for analyzing chemical kinetics in the photoreactor and the results were compared with experimental results for validating the model accuracy and the model showed good correlation. Results presented herein have demonstrated that VUV irradiation totally contributed H<sub>2</sub>O<sub>2</sub> formation and photodegradation by UV lights is negligible. It was demonstrated that both 'OH self-recombination and HO<sub>2</sub><sup>•</sup> and O<sub>2</sub><sup>•</sup> combination was contributed to  $H_2O_2$  formation and  $HO_2^{-}/O_2^{-}$ disproportionation was the reason of H<sub>2</sub>O<sub>2</sub> formation depending on initial pH. In addition,  $H_2O_2$  decreased under anoxic condition because presence or absence of DO changes the main reactant of H<sup> $\cdot$ </sup>. Not only that,  $H_2O_2$  was generated more as the concentration of organic matters increased. This study confirms that H<sub>2</sub>O<sub>2</sub> formation was affected by initial pH, DO, and organic matters concentration, and reaction of DO and H<sup>•</sup> is the most important one on H<sub>2</sub>O<sub>2</sub> formation. Furthermore, numerical simulation models were shown to be available for the analysis of mechanisms of complex chemical kinetics.

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초록

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임규승

최근 전기전자 산업의 규모가 증가함에 따라 반도체 및 디스플레이 제조공정에서 초순수의 수요가 늘어나고 있다. 원수는 초순수의 수질 조건을 충족하기 위해 정수처리, 역삼투압, 광산화 등 다양한 공정을 거치게 되는데, 이때 광산화 공정에서 발생하는 과산화수소가 문제가 될 수 있다. 광산화 공정의 경우 수중 용존유기탄소를 효과적으로 제거하기 위해 185-nm와 254-nm 파장의 빛이 나오는 VUV/UV 램프를 사용하는데, 185-nm 빛에 의해 물이 분해되어 생성된 라디칼들의 결합 반응에 의해 과산화수소가 생성된다. 초순수에 과산화수소가 잔류 할 시 반도체 웨이퍼를 산화시켜 제품의 품질에 악영향을 줄 수 있다. 많은 선행연구들이 과산화수소 생성 메커니즘을 실험적으로 규명하려 하였으나, 라디칼 반응의 경우 짧은 잔류시간으로 인해 정확한 분석이 어려워 아직 과산화수소 생성 메커니즘에 대해서는 정확히 밝혀져 있지 않다. 본 연구에서는 실험과 시뮬레이션을 융합하여 과산화수소 생성 메커니즘을 분석하였다. 용존 산소가 있을 경우 'OH 자가결합반응과 HO2' 그리고 O2' 결합 두 가지 반응 모두 과산화수소 생성에 중요한 영향을 주고, HO2'/O2' 불균등화 반응이 pH에 따른 과산화수소 농도

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변화에 대한 원인임을 제시한다. 유기물 농도가 증가하였을 때 과산화수소 생성이 증가하는 경향성은 HO<sub>2</sub>'그리고 O<sub>2</sub>' 결합에 의해 과산화수소가 생성됨을 뒷받침한다. 용존 산소가 없을 때 과산화수소가 생성되지 않고, 유기물 분해가 저해되는 결과는 산소와 'H의 반응이 과산화수소 생성에 매우 중요한 반응 임을 제시한다.

**주요어:** 시뮬레이션, 과산화수소, pH, 유기물, 용존 산소, OH **학번:** 2021-20093