Detection of Radicals and Reactive Species Formed in Wafer Cleaning Solutions Irradiated with Megasonic Waves

(*Task Number: 2324.001.)*

PIs:

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Other Researchers:

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Cost Share (other than core ERC funding):

- **Donation of Cavitation Threshold (CT) cell and MegBowl from *ProSys*, Inc., $30k**

Objectives and Methods of Approach

Objectives

- **Validate the existence of hydroperoxyl ($HO_2\cdot$) radicals in liquid medium irradiated by megasonic waves**
- **Quantify the rate of generation of H· radicals in a megasonic field**

Tasks

- ***Sub-task 1*: In-situ detection of $HO_2\cdot$ using a chemiluminescence (CL) technique**
- ***Sub-task 2*: Estimation of the generation rate of H· radicals in a megasonic field using chronoamperometry**

ESH Metrics and Impact

- **Control of concentration of active radicals through megasonic input would allow *in situ* generation of cleaning power, thus leading to reduction in the use of "bulk" cleaning chemicals.**

Sub-task 1: In-situ detection of HO_2· using a chemiluminescence (CL) technique

Method of Approach

- **Detection of hydroperoxyl radicals was done using a chemiluminescence (CL) method; MCLA (2-methyl-6-(p-methoxyphenyl)-3,7-dihydroimidazo[1,2-a]pyrazine-3-one) was used as the CL probe* .**

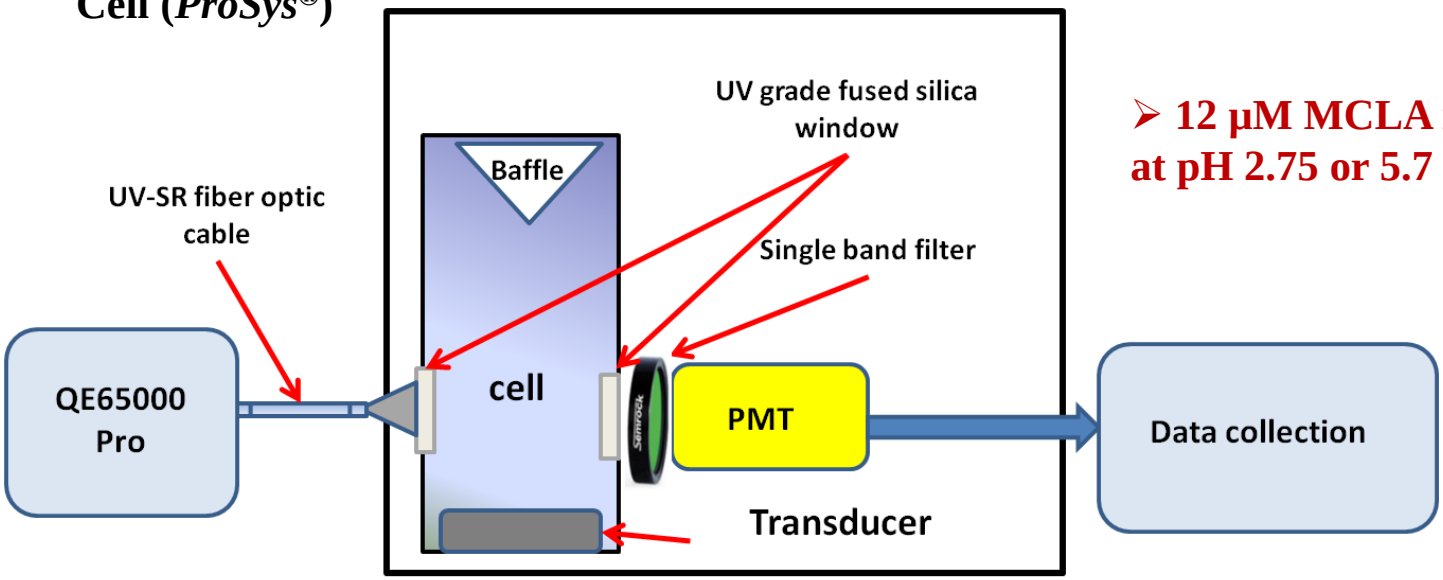
- **The complex between MCLA and hydroperoxyl radical emits light in the wavelength range of 457 to 465 nm.**

- **CL emission was captured and analyzed by a spectrometer**

*Y. Kambayashi and K. Ogino, Reestimation of cypridina luciferin analogs (MCLA) as a chemiluminescence probe to detect active oxygen species, J of Toxicological Sciences, Vol. 28 (3), pp. 139-148 (2003)

Schematic of the Experimental Set-up

Cavitation Threshold (CT) Cell (*ProSys*®)



➢ **12 µM MCLA in 1:100 ethanol : DIW at pH 2.75 or 5.7**

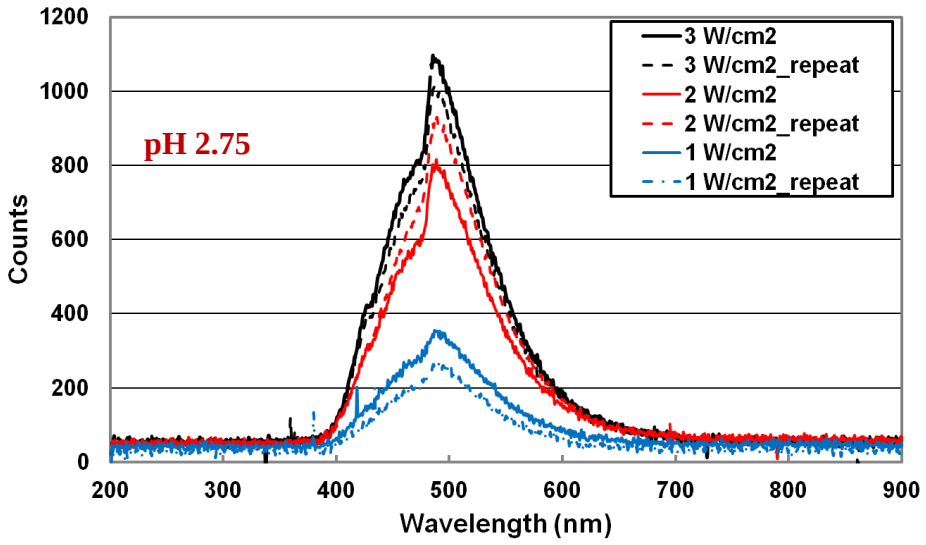
CT Cell Details

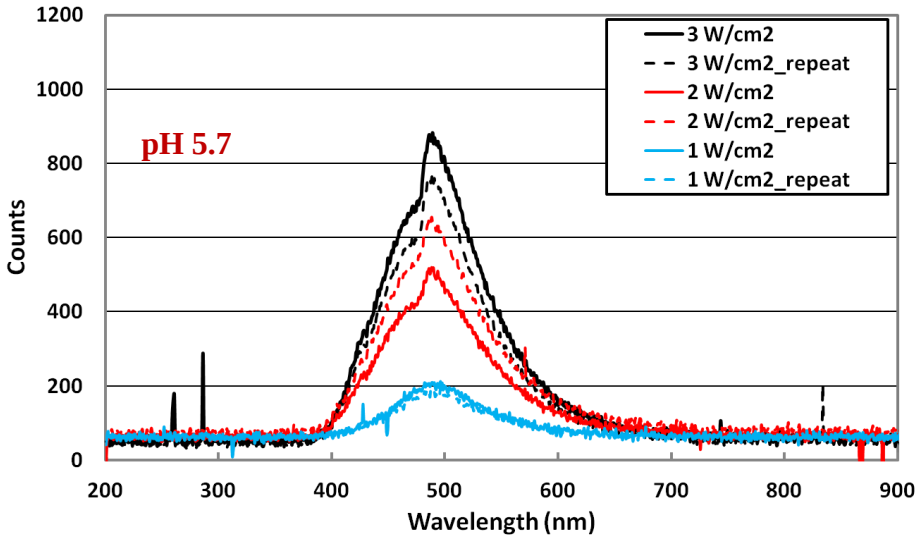
- ***Volume = 163 cc, Length = 10.4 cm***
- ***Internal Diameter = 4.8 cm***
- ***Sonic Frequency = 0.925 MHz***
- ***PMT Wavelength Range = 280 to 630 nm***
- ***Power Density Range = 0.1 to 4 W/cm²***

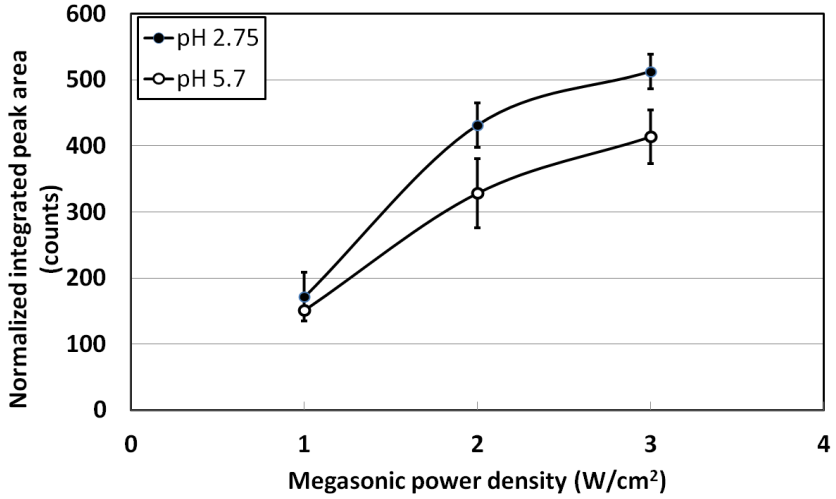
- **Spectrometer: QE65000 Pro (Ocean Optics)**
- **FO cable: UV-SR (11 cm)**
- **Spectral acquisition time: 2 min**
- **Single band filters:**

1. **300~340 nm**
2. **432~482 nm**

Effect of Megasonic Power Density on CL Intensity

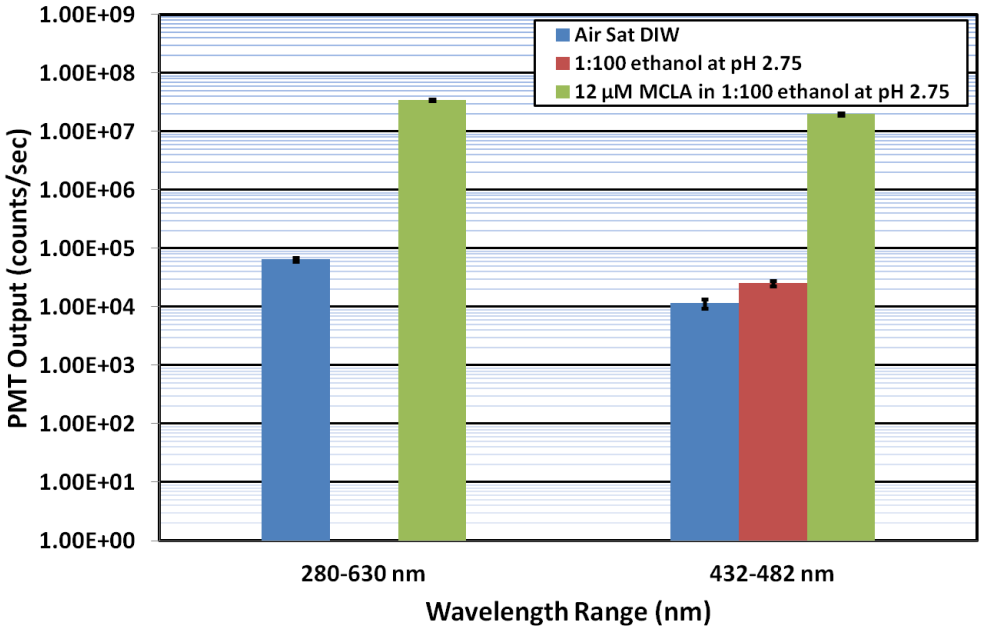






- **The intensity of CL is a function of megasonic power density and solution pH**
- **Emission peak at 480 nm**
- **Results confirm the existence of HO_2·**

Confirmation of Emission from MCLA Complex with Hydroperoxyl Radicals from Sonoluminescence Signal Measured using PMT



1 W/cm^2

- **In solutions containing MCLA, PMT output is dominated by emission in the wavelength range of 432 to 482 nm; this proves the existence of MCLA-$HO_2^{\cdot}$ complex**

Sub-task 2: Estimation of the generation rate of H· radicals in a megasonic field using chronoamperometry

Method of Approach

- **Hydrogen radicals (H·) generated during megasonic irradiation can reduce Cu^{2+} ions to cuprous ions (Cu^{+}); in the presence of excess chloride ions, Cu^{+} will be converted to $CuCl_2^-$**

$$H_2O \longrightarrow H^{\bullet} + OH^{\bullet}$$

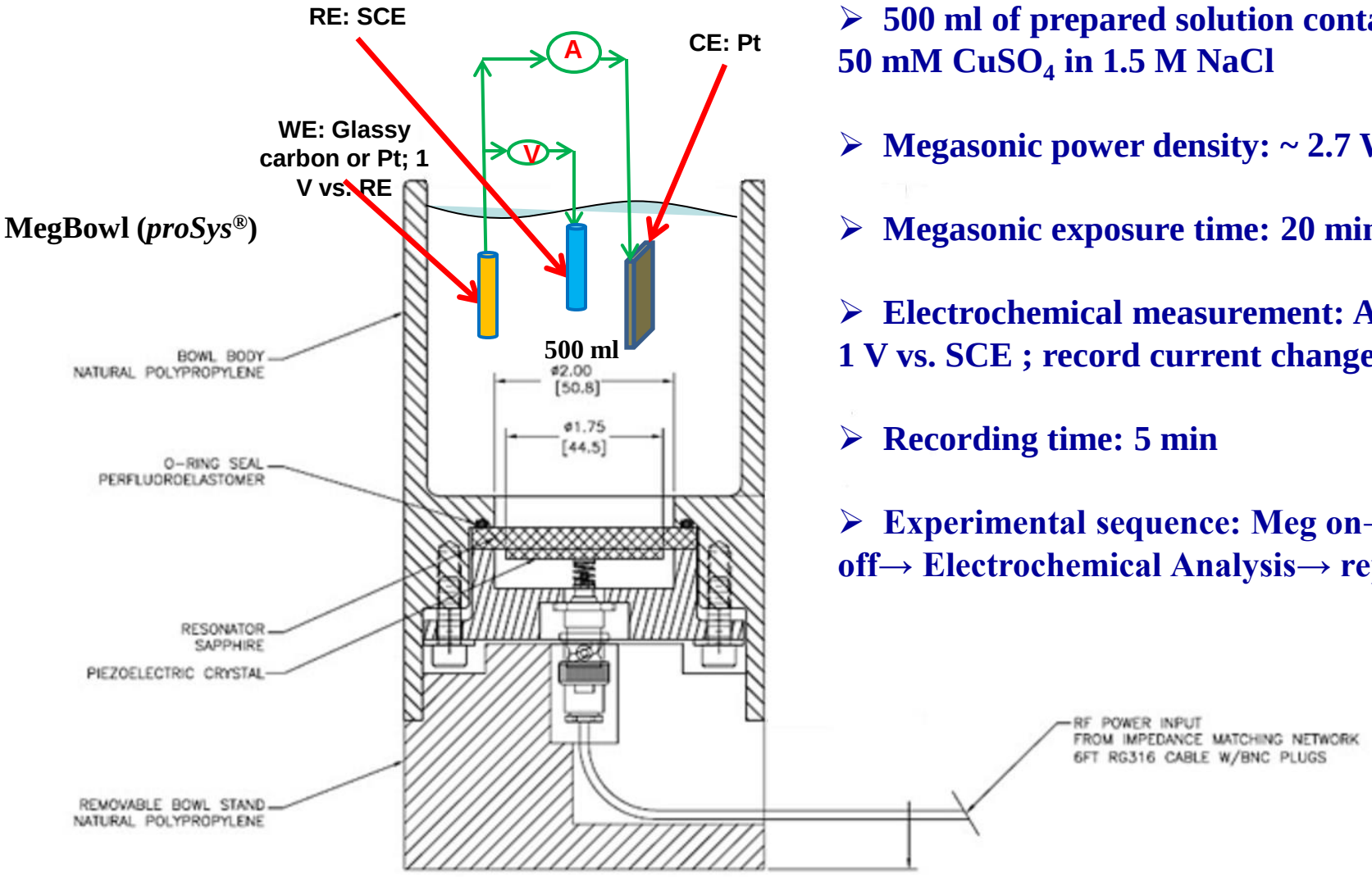
$$Cu^{2+} + H^{\bullet} \longrightarrow Cu^{+} + H^{+} \qquad Cu^{+} + 2Cl^{-} \longrightarrow CuCl_2^{-}$$

- **Generation rate of $CuCl_2^-$ is equal to the generation rate of H· (assuming no other routes exist for the consumption of H·)**

- **$CuCl_2^-$ can be measured by electrochemical oxidation to Cu^{2+}**

P. R. Birkin, J. F. Power and T. G. Leighton, Electrochemical evidence of H· by ultrasound, Chem. Commun., pp. 2230-2231 (2001)

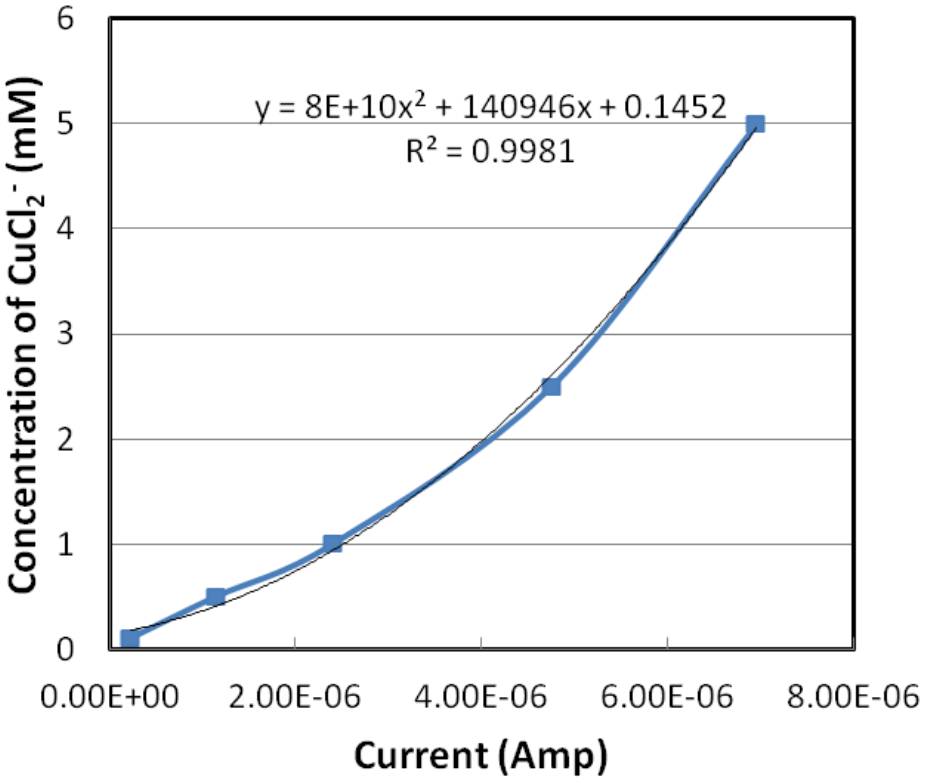
Schematic of Electrochemical Set-up in MegBowl



- 500 ml of prepared solution containing 50 mM $CuSO_4$ in 1.5 M NaCl
- Megasonic power density: ~ 2.7 W/cm^2
- Megasonic exposure time: 20 min
- Electrochemical measurement: Apply 1 V vs. SCE ; record current change
- Recording time: 5 min
- Experimental sequence: Meg on→ Meg off→ Electrochemical Analysis→ repeat

Calibration Curve for $CuCl_2^-$

Concentration of $CuCl_2^-$ (mM)	Current at 300 sec (Amp)
5	6.95±0.45E-06
2.5	4.75±0.01E-06
1	2.40±0.13E-06
0.5	1.15±0.02E-06
0.1	2.25±0.03E-07



- **Standard solutions containing $CuCl_2^-$ were prepared from CuCl(s)**

Calculated H· Generation Rate in 50 mM $CuSO_4$ solution When exposed to Megasonic Field at 2.7 W/cm^2

Megasonic exposure time (min)	Current at 300 sec (Amp)	$CuCl_2^-$ concentration (mM)	$CuCl_2^-$ generation rate (mM/s)	$CuCl_2^-$ generation rate (nM/s)	H· generation rate (nM/s)	Solution temp. (degree C)
20	6.35E-07	2.67E-01	8.12E-05	~ 80	71 ± 12	42.0
	5.28E-07	2.42E-01	7.54E-05	~ 75		42.0
	4.35E-07	2.22E-01	5.79E-05	~ 58		41.2

- H· generation rate in the range of 71±12 nM/s at 2.7 W/cm^2
- After 20 min megasonic exposure, solution temperature increased to be ~ 40 degree C
- In 125 Hz ultrasonic field, the generation rate of H· has been reported to be 400 nM/s at 6 W/cm^2

Summary

- **Developed an *in-situ* chemiluminescence (CL) based detection method for $HO_2\cdot$ generated in megasonic field. CL intensity increases with megasonic power density.**

- **Using an electrochemical method, estimated the generation rate of H· in 2.7 W/cm^2 megasonic field to be 70±10 nM/s.**

Industrial Interactions and Technology Transfer

- **Technical discussions with Dr. Ian Brown (TEL/AMAT)**

Future Plans

Plans for the remainder of the contract period

- **Measure the generation rate of hydrogen radicals in basic cleaning solutions at different power densities**

Publications, Presentations, and Recognitions/Awards

- **M. Keswani, S. Raghavan, R. Govindarajan and I. Brown, Measurement of hydroxyl radicals in wafer cleaning solutions irradiated with megasonic waves, *Microelectronic Engineering* (2013), in press, http://dx.doi.org/10.1016/j.mee.2013.12.028.**

- **Z. Han and S. Raghavan, *In-situ* chemiluminescence (CL) based detection and quantitation of hydroperoxyl radicals in aqueous solutions under megasonic irradiation, invention disclosure filed with Tech Launch Arizona.**

- **M. Keswani, S. Raghavan, I. Brown, Measurement of hydroxyl radicals in wafer cleaning solutions irradiated with megasonic field, presented at Sematech *SPCC* conference, Austin, TX, Apr. 4th, 2013.**