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

(*Task Number: 2324.001.)*

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- **Manish Keswani, Postdoctoral Fellow, *Currently Assistant Professor in Materials Science and Engineering, UA***

Cost Share (other than core ERC funding):

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

Objectives

Project Duration	Objective	Publication
July 2012~June 2013	Determination of Hydroxyl Radical (OH•) Generation Rate (presented at 2013 Annual Review)	1
July 2013~June 2014	Measurement of Hydrogen Radical (H•) Generation Rate (presented at 2014 Annual Review)	
	Detection of Hydroperoxyl Radical (HO_2•) (presented at 2014 Annual Review)	1
	Quantitation of Hydroperoxyl Radical (HO_2•) Generation Rate	

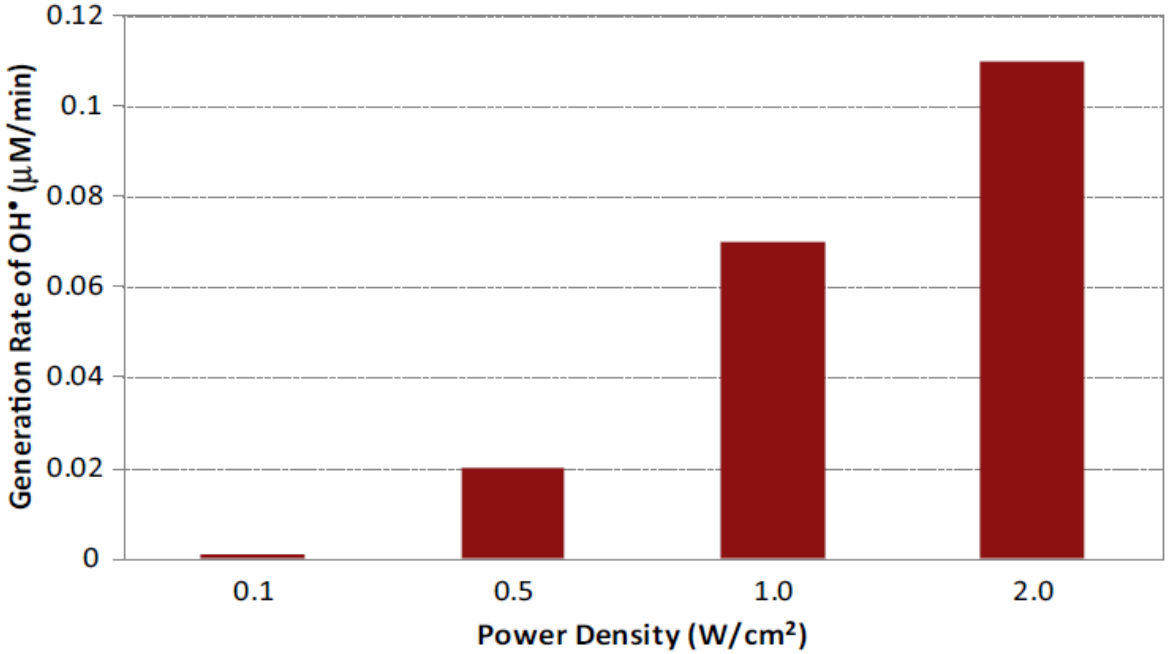
ESH Metrics and Impact

- **Generation of active radicals through the application of megasonic energy to liquid chemical formulations would create *in situ* generation of cleaning power, thus leading to reduction in the use of "bulk" cleaning chemicals.**

Sub-task 1: Determination of OH• Generation Under Megasonic Irradiation

Method of Approach

Determination of OH• generation rate was done employing fluorescence spectroscopy using terephthalic acid as a probe.



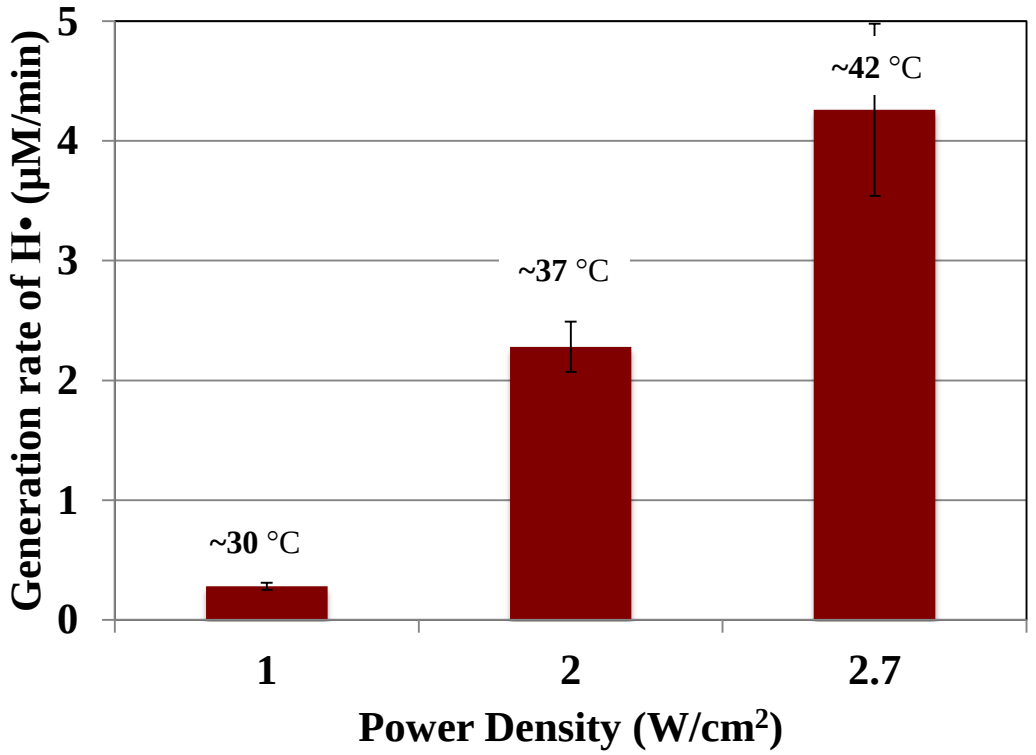
Effect of transducer power density on generation rate of hydroxyl radicals in air saturated 1:10000 NH_4OH (29%):H_2O solutions of pH 10 at 25 °C.

Ref: M. Keswani et al, Microelectronic Engineering 118 (2014) 61–65

Sub-task 2: Measurement of H• Generation Rate in a Megasonic Field

Method of Approach

Measurement of H• was done through the reduction of Cu^{2+} in the presence of excess chloride ions followed by chronoamperometry



Sub-task 3: Detection and Quantitation of HO_2• Generation under Megasonic Irradiation

Method of Approach

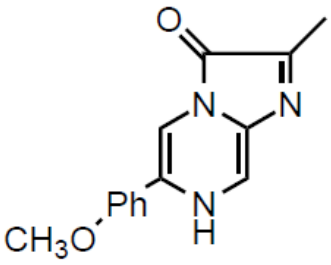
- **Detection of hydroperoxyl radicals was done emlopying a chemiluminescence (CL) method using MCLA as a CL probe**

- **Quantitation of hydroperoxyl radicals was done utilizing the redox reaction between hydroperoxyl radicals and cytochrome *c***

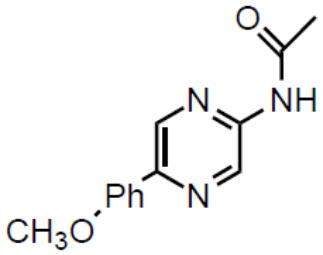
Detection of $HO_2\bullet/O_2\bullet^-$ Using Chemiluminescence (CL)

- **MCLA (*2-methyl-6-(p-methoxyphenyl)-3,7-dihydroimidazo[1,2-a]pyrazine-3-one*), also known as "Methyl Cypridina Luciferin Analogue"**
- **The complex between MCLA and $HO_2\bullet/O_2\bullet^-$ radicals emits light in the wavelength range of 457 to 465 nm.**

$$MCLA + HO_2 \cdot / O_2 \cdot^- \rightarrow \cdots \rightarrow OxyMCLA + h\upsilon(457nm)$$



MCLA



OxyMCLA

Ref: Y. Kambayashi and K. Ogino, J. of Toxicological Sci. 28 (2003), p. 139.

Quantitation of $HO_2\bullet/O_2\bullet^-$ Radicals Using Ferricytochrome *c* (Fe^{III}cyt *c*)

Oxygen anion radical can be oxidized by Fe^{III}cyt *c*

$$Fe^{III}\text{cyt } c + e \rightarrow Fe^{II}\text{cyt } c$$

E° (Fe^{III}cyt *c*/Fe^{II}cyt *c*) = +0.26 V

$$e + O_2 \rightarrow \bullet O_2^-$$

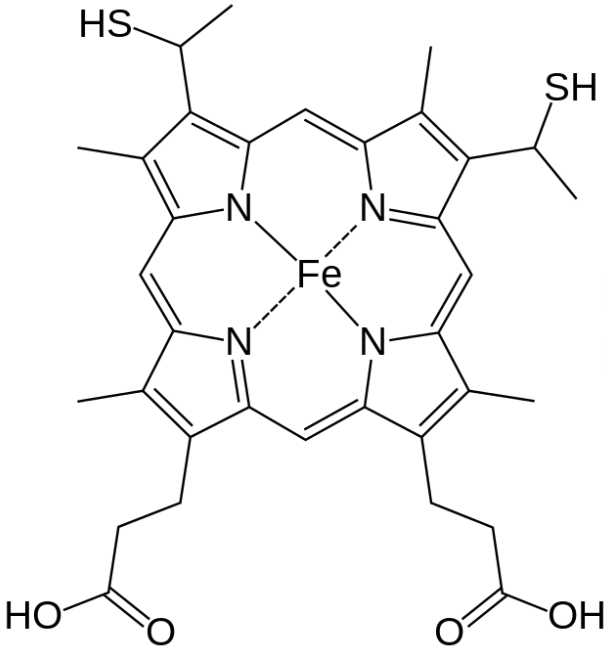
E° ($O_2/\bullet O_2^-$) = -0.33 V

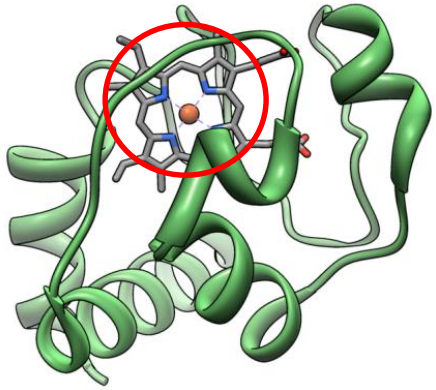
OVERALL REACTION

$$Fe^{III}\text{cyt } c + \bullet O_2^- \rightarrow Fe^{II}\text{cyt } c + O_2$$

E^0_{cell}=0.59 V

Structure of cytochrome *c*

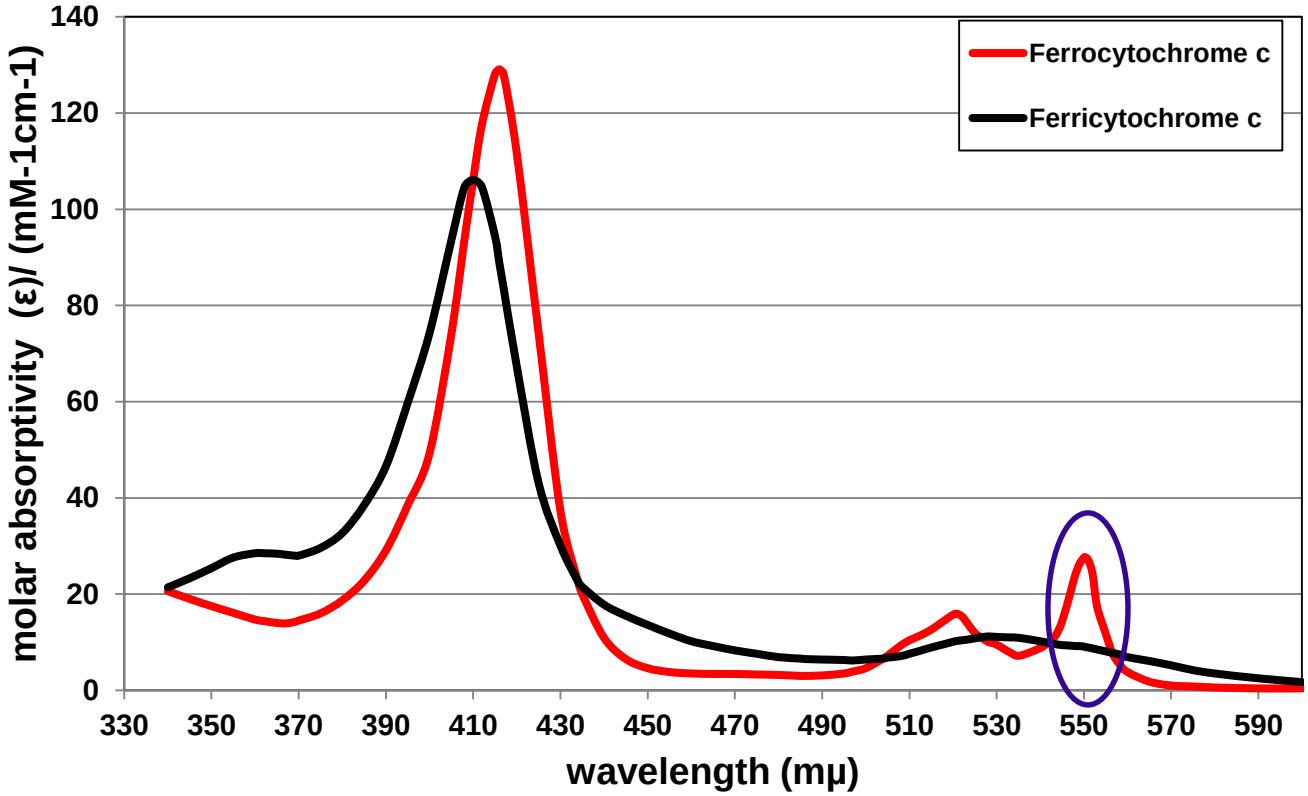




P. Muirwood, FEBS Lett. 44 (1974), p. 22-24.
R. Margalit, A. Schejter, European Journal of Biochemistry. 32 (1973), p. 492-499.

Quantitation of $HO_2\bullet/O_2\bullet^-$ Radicals by Reaction with Ferricytochrome *c* (Fe^{III}cyt *c*)

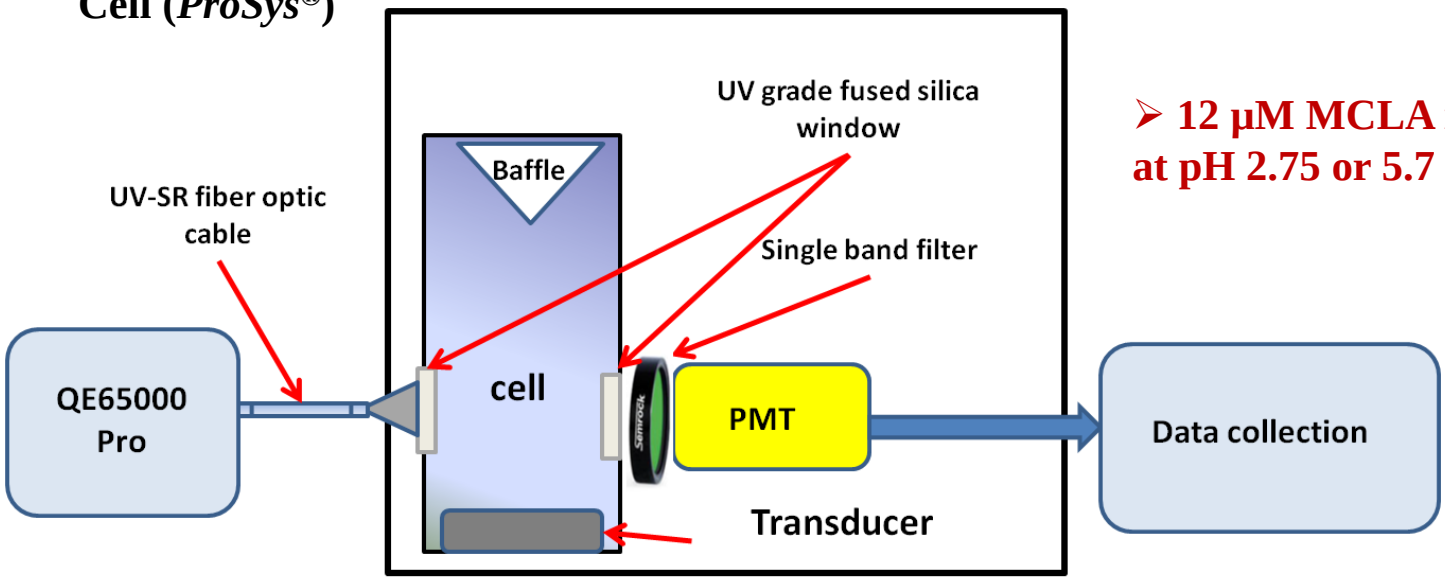
Characteristic peak appears at about 550 nm when cytochrome *c* is reduced



Plotted from MARGOLIASH, E, BIOCHEMICAL JOURNAL, 71 (1959), p. 570-578

Experimental Set-up for HO_2• Detection

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



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

CT Cell Details

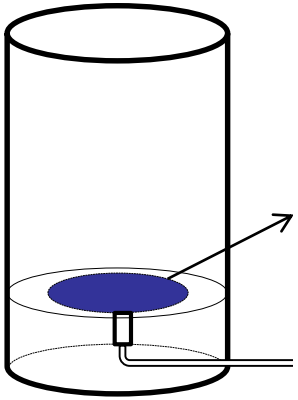
- ***Volume = 163 cc, Length = 10.4 cm***
- ***Internal Diameter = 4.8 cm***
- ***Sonic Frequency = 0.925 MHz***
- ***PMT Wavelength Range = 280 to 630 nm***
- ***Power Density Range = 0.1 to 4 W/cm²***

- **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**

Experimental Setup for Quantitation of $HO_2•/O_2•^-$

Bowl Meg (*ProSys*®)



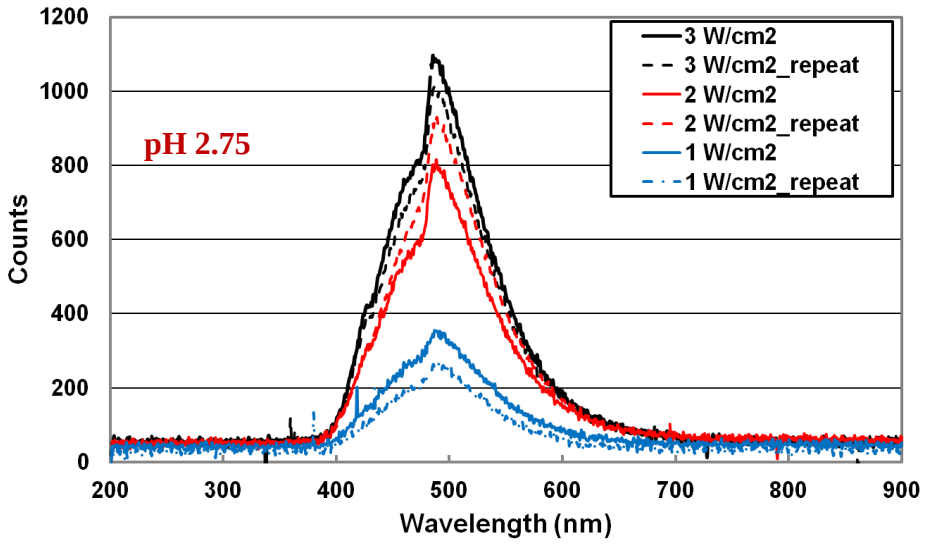
Transducer, Diameter ~ 4.5 cm: f =0.93MHz

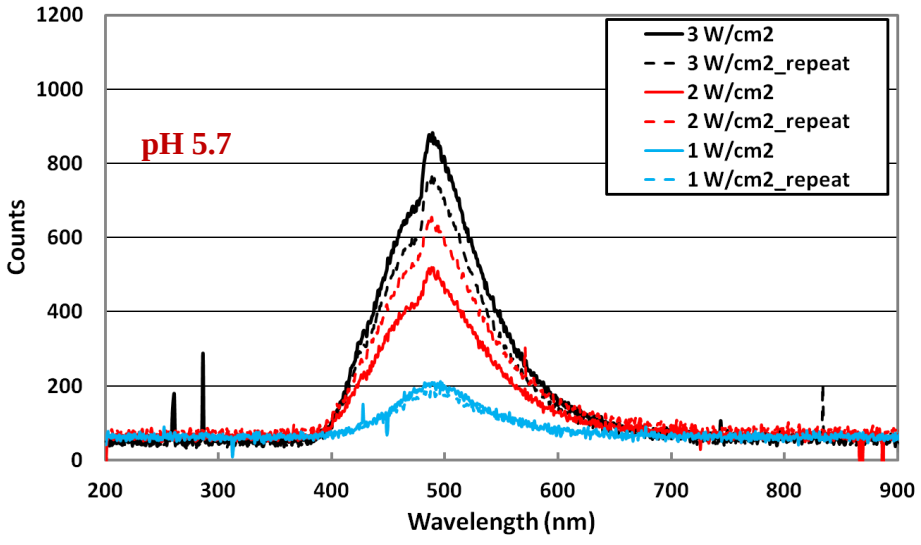
RF power input

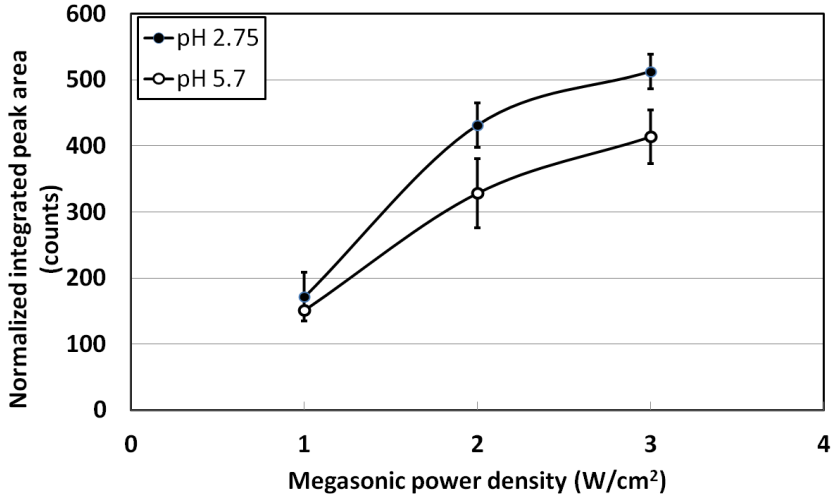
UV-VIS-NIR Spectrophotometer (Shimadzu® UV-3100)

- **Ferricytochrome *c* in 0.1M buffered sodium formate solution at pH=7 was exposed to megasonic irradiation**
- **Samples were collected at different times for spectrophotometric analysis using Shimadzu UV-3100 spectrometer**

Detection: Effect of Megasonic Power Density on CL Intensity

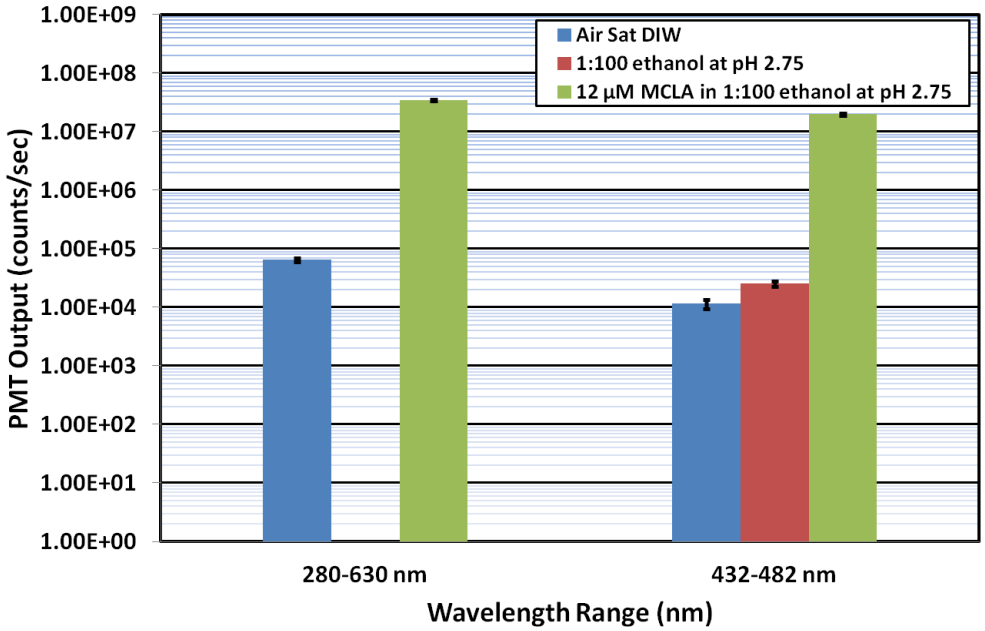






- The intensity of CL is a function of megasonic power density and solution pH
- Emission peak at ~490 nm
- Results confirm the existence of HO_2•

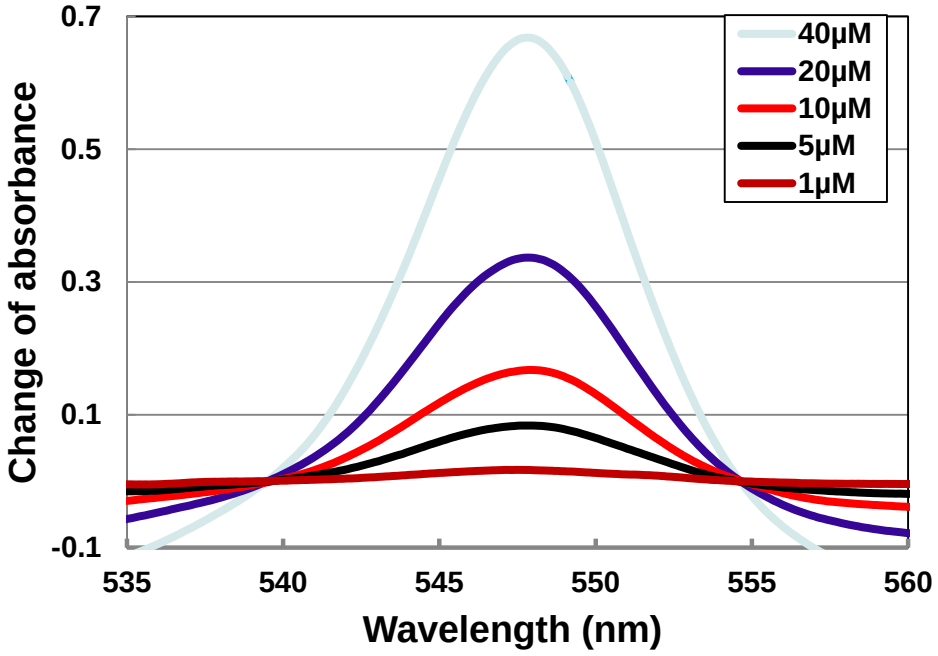
Confirmation of Emission from MCLA Complex with Hydroperoxyl Radicals from Sonoluminescence Signal Measured using PMT

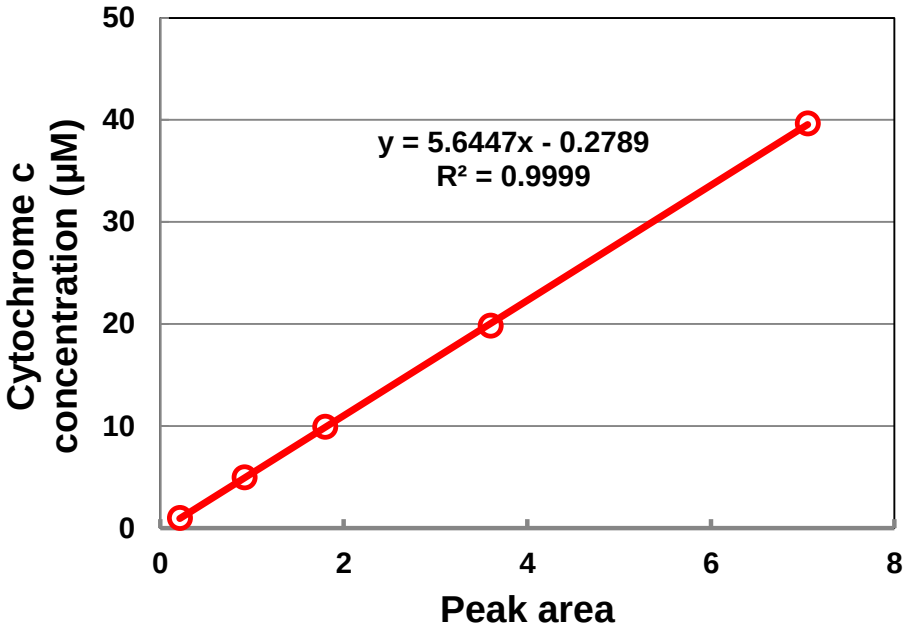


1 W/cm^2

- **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• complex**

Quantitation: Calibration Curve

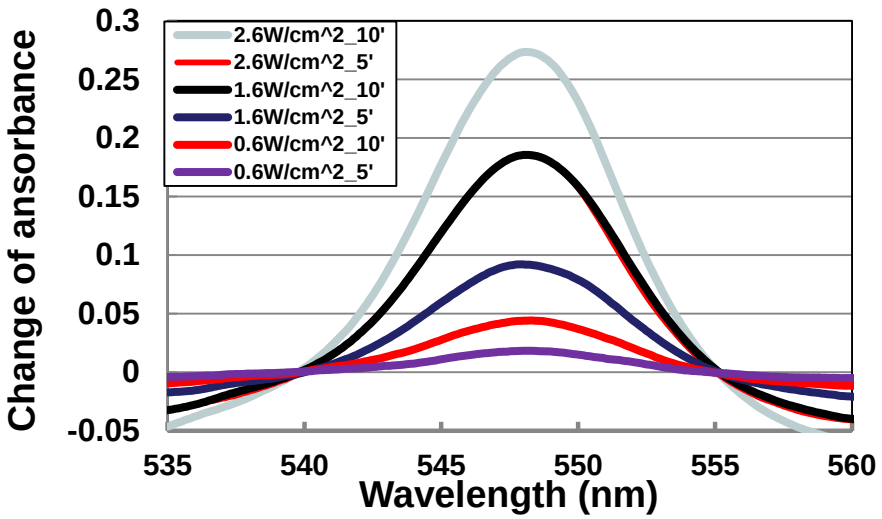


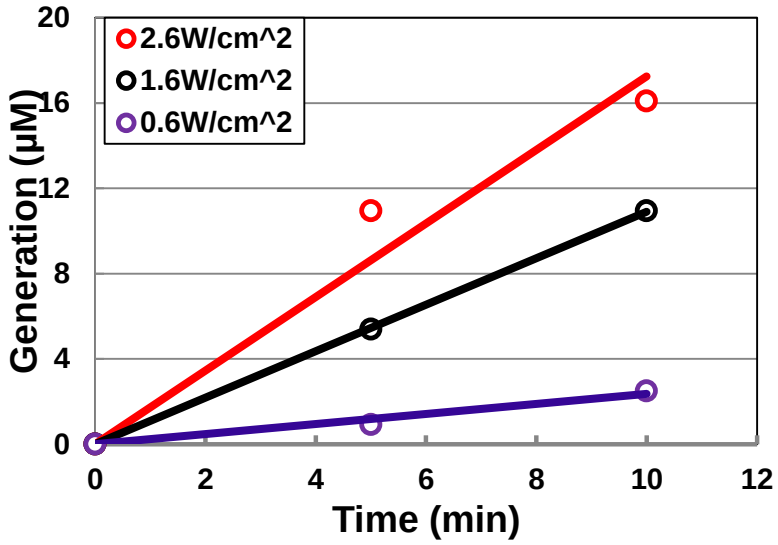


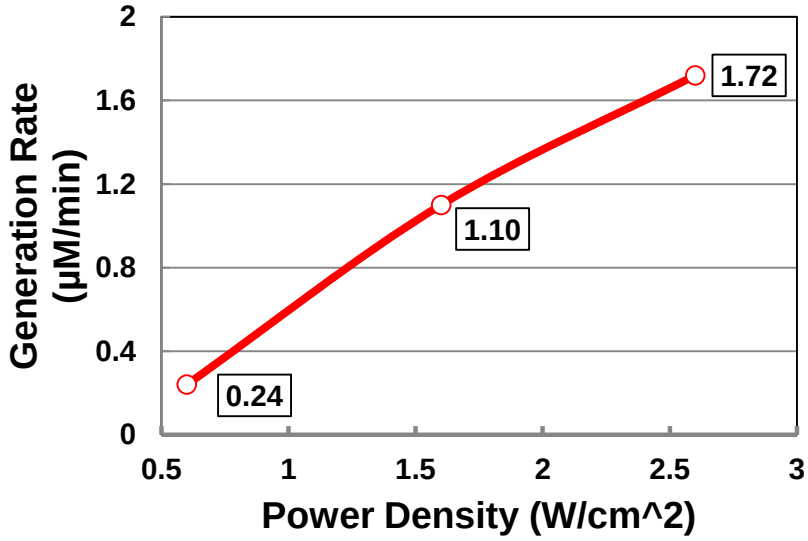
- The "change of absorbance" is defined as the difference between the absorbance spectra of ferrocytochrome *c* and ferricytochrome *c*

- Peak area at ~548 nm is proportional to Ferri cytochrome *c* concentration

Quantitation: Effect of Power Density on Generation of $HO_2\bullet/O_2\bullet^-$







➢ **Generation rate of $HO_2\bullet/O_2\bullet^-$ Radicals increases with power density**

Summary

- **Measured OH• generation rate using fluorescence spectroscopy technique**

- **Measured H• generation rate using chronoamperometry**

- **Developed an *in-situ* chemiluminescence (CL) based detection method for HO_2• generation; quantified HO_2• generation rate through the extent of reduction of ferricytochrome-c**

Industrial Interactions and Technology Transfer

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

Publications, Presentations, and Recognitions/Awards

Publications

- **M. Keswani, S. Raghavan, R. Govindarajan, I. Brown, Measurement of hydroxyl radicals in wafer cleaning solutions irradiated with megasonic waves, *Microelectronic Engineering*. 118 (2014) 61-65.**
- **Z. Han, B. Wu, I. Brown, M.Beck and S. Raghavan, Detection of $HO_2\bullet/O_2\bullet^-$ Radicals Formed in Aqueous Solutions Irradiated with Megasonic Waves using a Cavitation Threshold (CT) Cell Set-up, *Solid State Phenomena*. 219 (2015) 170-173**
- **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.**

Presentations

- **Z. Han, B. Wu, I. Brown, M. Beck and S. Raghavan, Detection of $HO_2\bullet/O_2\bullet^-$ Radicals Formed in Aqueous Solutions Irradiated with Megasonic Waves using a Cavitation Threshold (CT) Cell Set-up, presented at the *12th International Symposium on Ultra Clean Processing of Semiconductor Surfaces (UCPSS)*, Brussels, Belgium, Sept. 21-24, 2014.**
- **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.**