Measurement of Hydroxyl Radicals in Wafer Cleaning Solutions Irradiated with Megasonic Field

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Introduction

- Megasonic irradiation of liquids is known to generate free radicals

- Traditionally, formation of hydroxyl radical ($OH^{\bullet}$) in acoustically irradiated solutions has been qualitatively identified using sonoluminescence spectrum

- Limited studies on measurement of $OH^{\bullet}$ concentration have focused on aqueous solutions of near neutral pH with megasonic (~1-3 MHz) exposure using a sonic probe

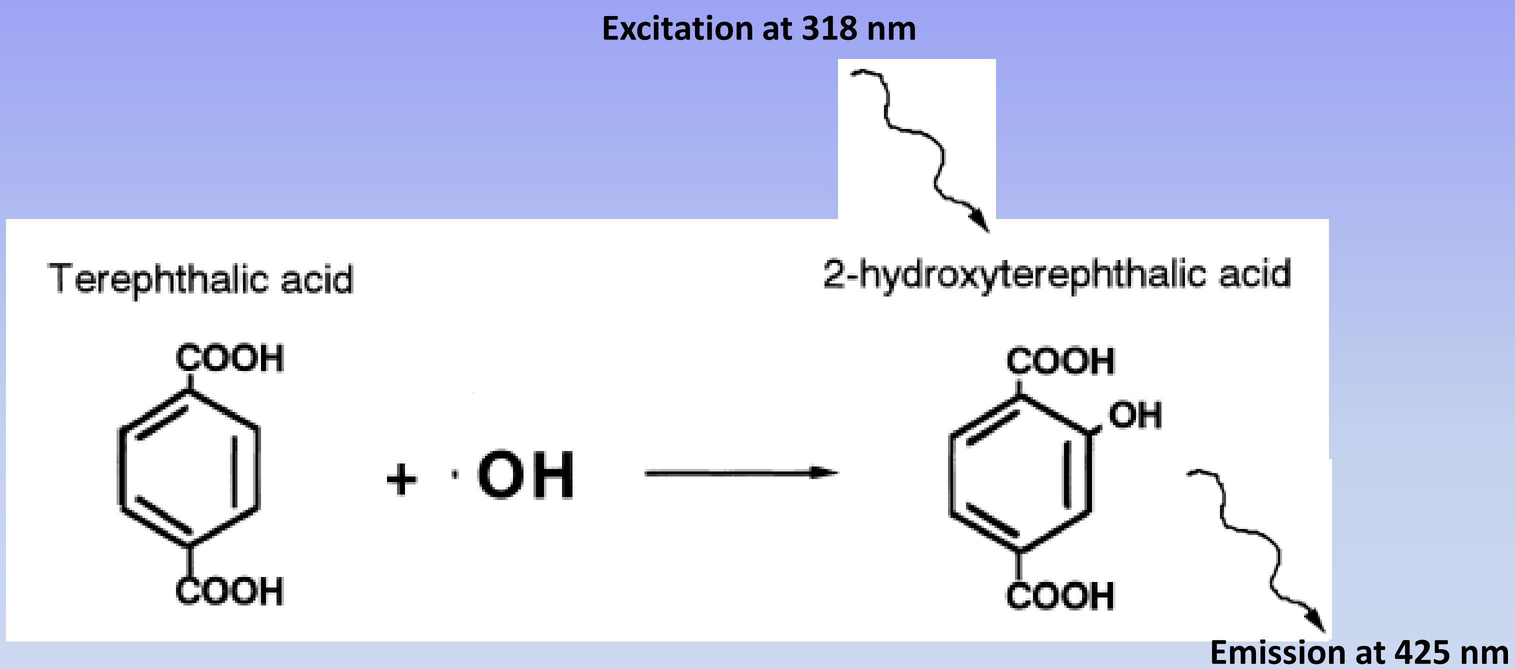
- Since $OH^{\bullet}$ have strong oxidizing potential, systematic Investigations of hydroxyl radical generation in wafer cleaning solutions using immersion and single wafer meg systems would be of interest to semiconductor industry

Key Objective and Approach

- **Key Objective :**
  - Measure concentration of hydroxyl radicals generated in megasonic irradiated solutions under immersion and single wafer cleaning conditions

- **Approach:**
  - Fluorometric technique based on complexation of OH radicals by terephthalic acid
  - Key experimental variables investigated: solution pH, temperature, type and concentration of dissolved gases, transducer power density and exposure time

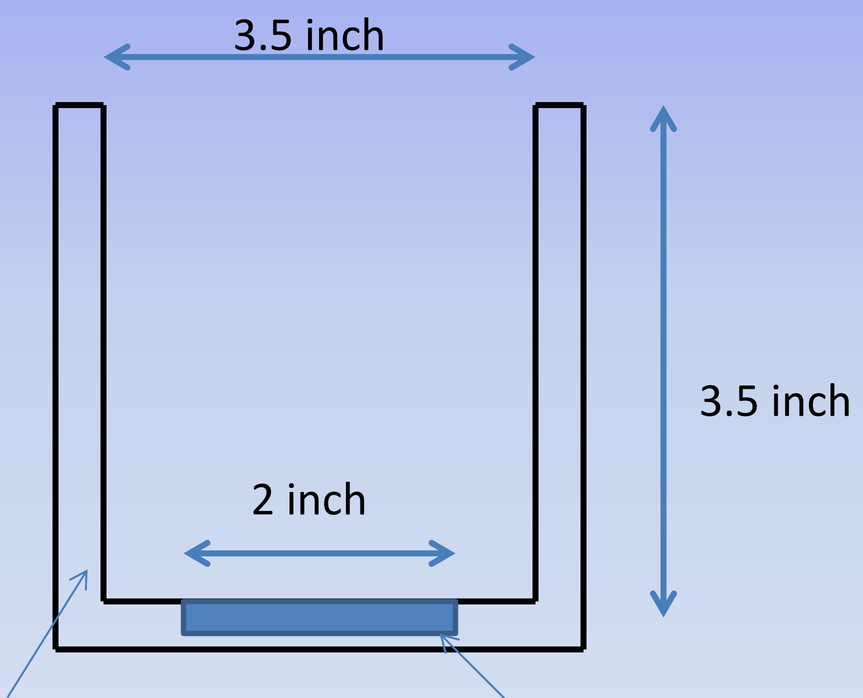
Fluorescence Spectroscopy Using Terephthalic Acid



- ➢ **Hydroxyl radical trapped using terephthalic acid to form 2-hydroxyterephthalic acid, measured using using fluorescence spectroscopy**
- ➢ **2-hydroxyterephthalic acid is stable up to 6 hours at room temperature**

Megasonic Systems (ProSys) Used for Experimental Investigations

Megbowl® – Immersion type (~ 1 MHz freq. 0.1-2.0 W/cm² power density)

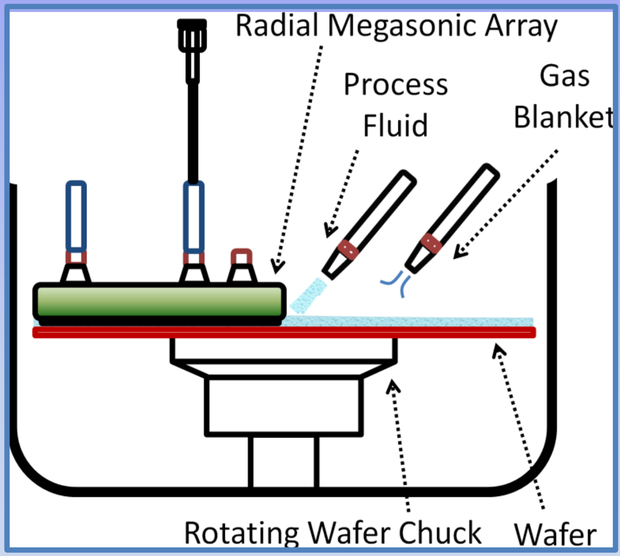


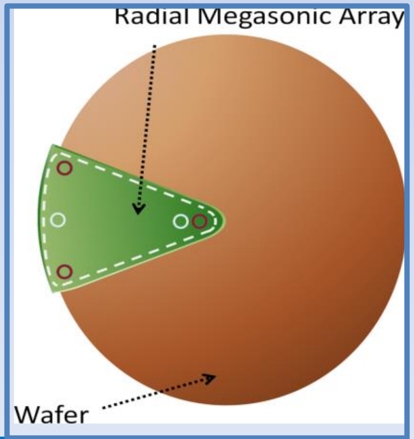
polypropylene

circular transducer with sapphire resonator on top

Megbowl® and MegPie® are registered trademarks of ProSys (Campbell, CA)

MegPie® – Single wafer (~ 1 MHz freq. 0.1-3.0 W/cm² power density)





Experimental Procedures

- Chemical/gas of interest (Ar, CO_2, NH_4OH, TMAH, KOH, or phosphate buffer) was bubbled/added to achieve desired composition and pH. Solution heated/cooled to a different temperature if desired. Solution was air saturated unless stated otherwise

- All solutions contained ~ 75 μM of Terephthalic acid

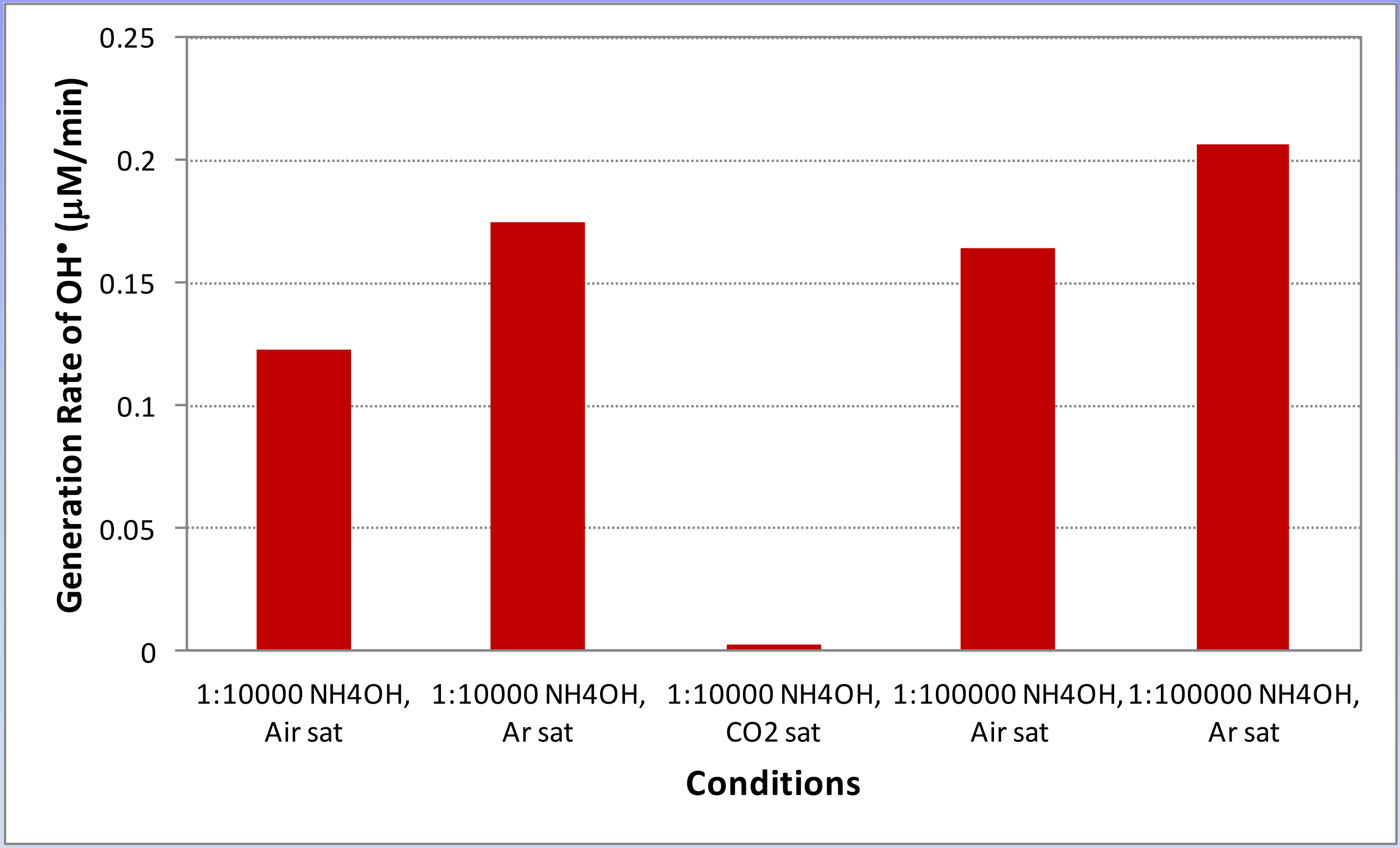
- Solutions subjected to ~ 1 MHz sound field at 0.1 to 2 W/cm^2 (**ProSys Megbowl® or MegPie®**) for different times at 25 deg C (unless stated otherwise).

- Fluorescence intensity measured at 425 nm (excitation at 318 nm) using RF-5301PC Spectrofluorometer

- For calibration, solutions containing hydroxy terephthalic acid instead of terephthalic acid were used

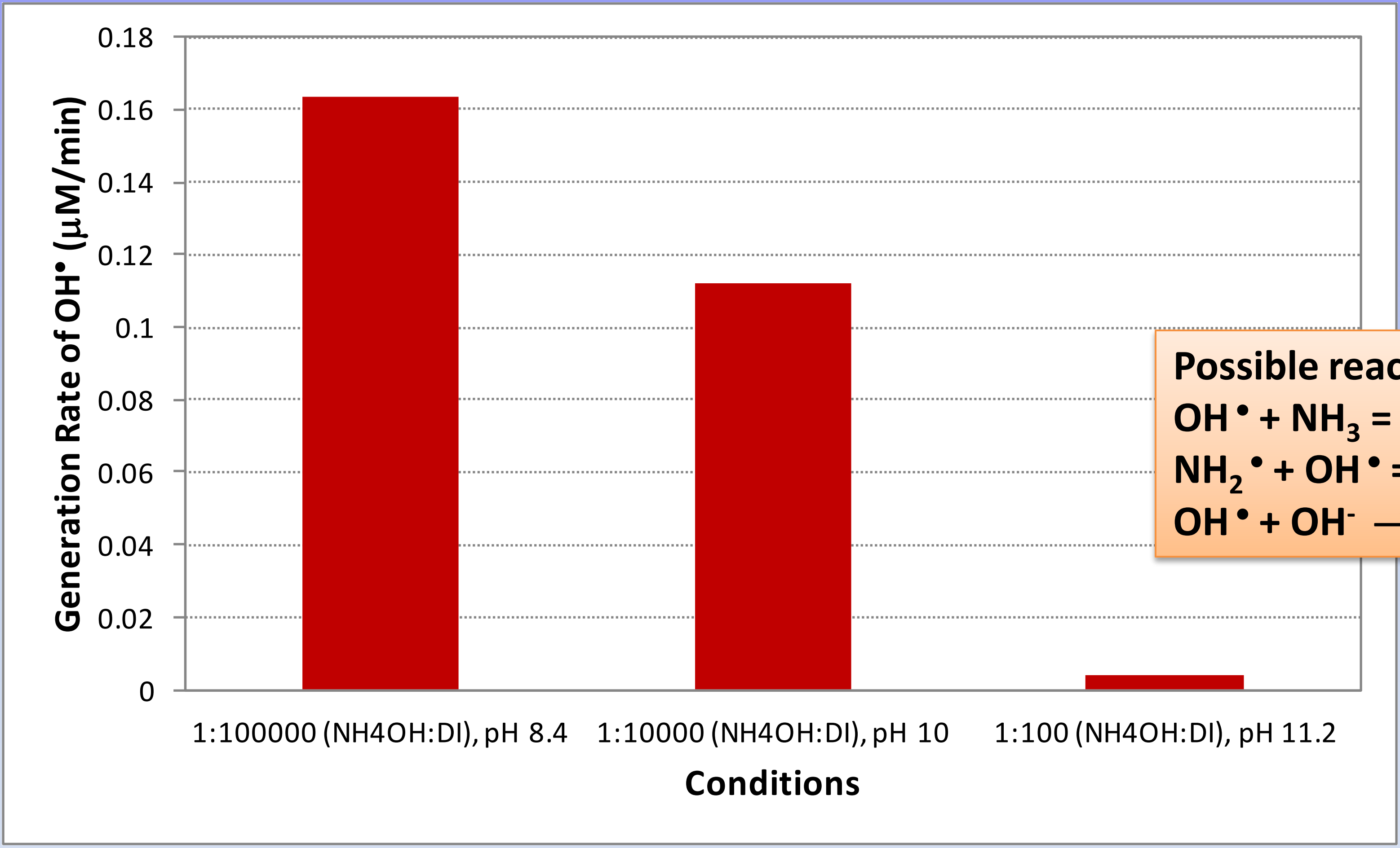
Phase I- Experimental Investigations in Immersion Meg System

Effect of Dissolved Gases on Hydroxyl Radical Generation in NH_4OH solutions at 2 W/cm^2



- **Hydroxyl radical generation higher in Ar saturated solutions compared to air saturated solutions**
- **No measureable OH• conc. in CO_2 saturated solutions**

Effect of Ammonia on Hydroxyl Radical Production at Megasonic Power Density of 2 W/cm^2



Possible reactions:

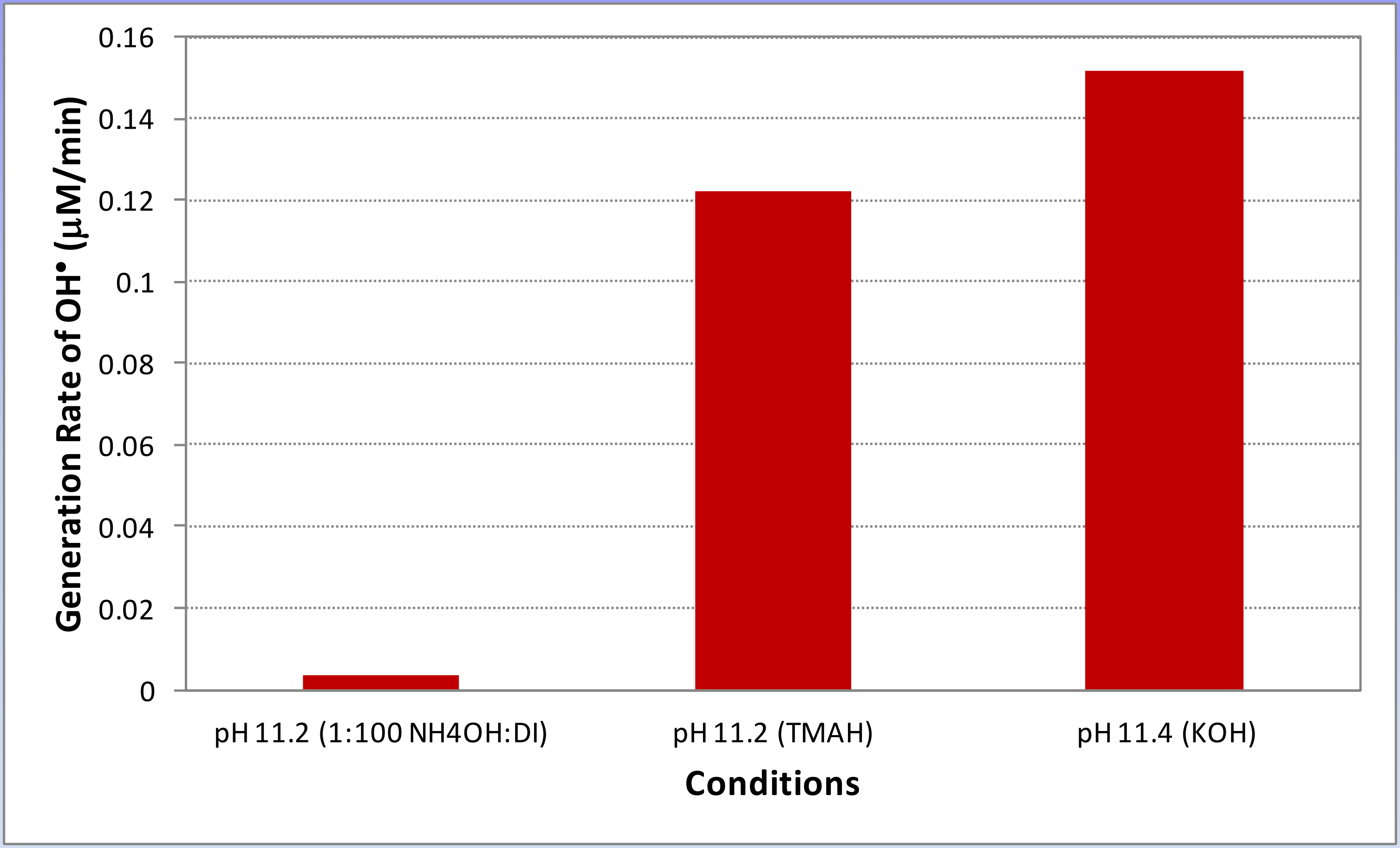
$OH^{\bullet} + NH_3 = NH_2^{\bullet} + H_2O$

$NH_2^{\bullet} + OH^{\bullet} = NH_2OH$

$OH^{\bullet} + OH^{-} \rightarrow O^{\bullet -} + H_2O$

Generation rate of OH• decreases with increase in NH_4OH concentration

Effect of pH on Hydroxyl Radical Production at Megasonic Power Density of 2 W/cm^2

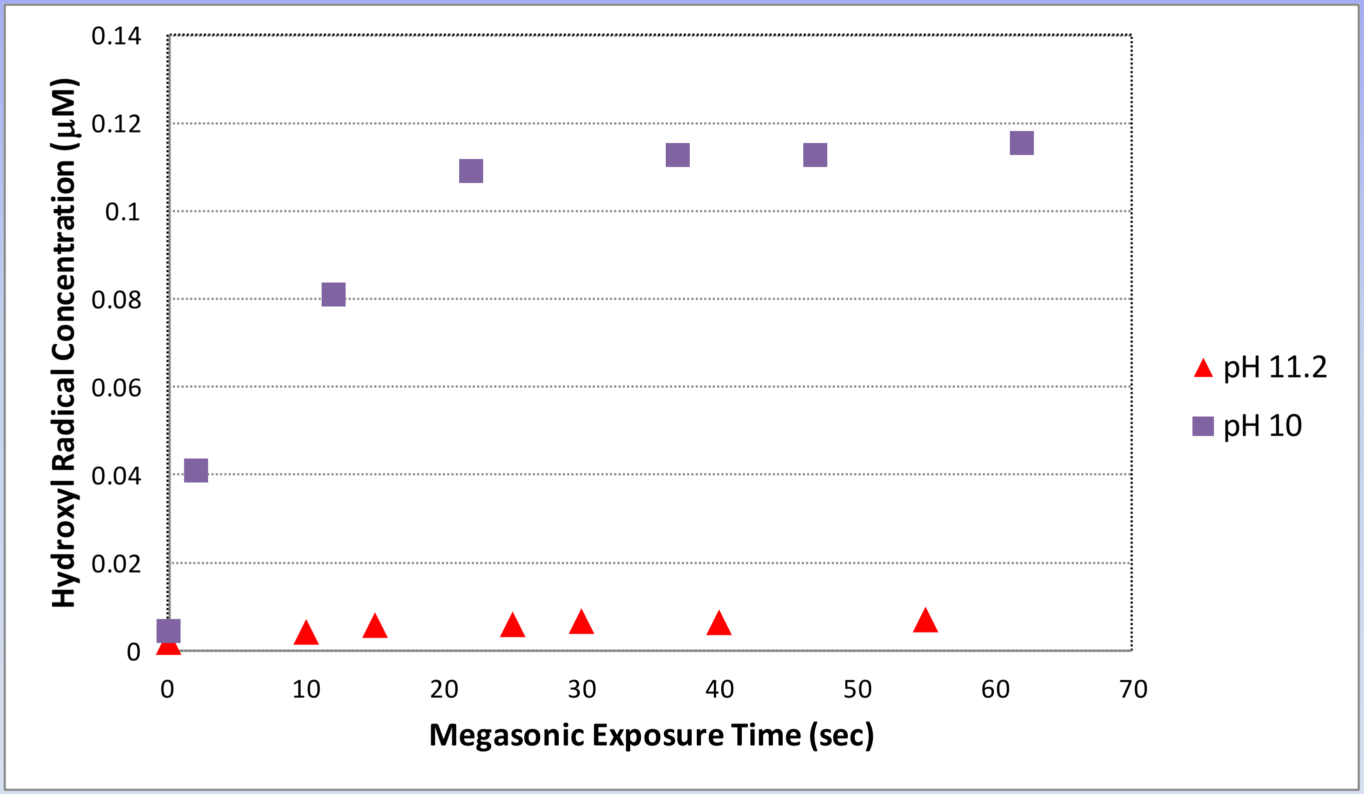


At pH ~11.2, generation rate of OH• depends on type of alkali used

Phase II- Experimental Investigations in Single wafer Meg System

Effect of Ammonia on Hydroxyl Radical Production at Megasonic Power Density of 2 W/cm^2

- Dispense ammonical solutions containing terephthalic acid at 300 ml/min on 8" Si water rotating at 30 rpm
- Start meg exposure after 5 s, collect samples from effluent streams and analyze for OH•



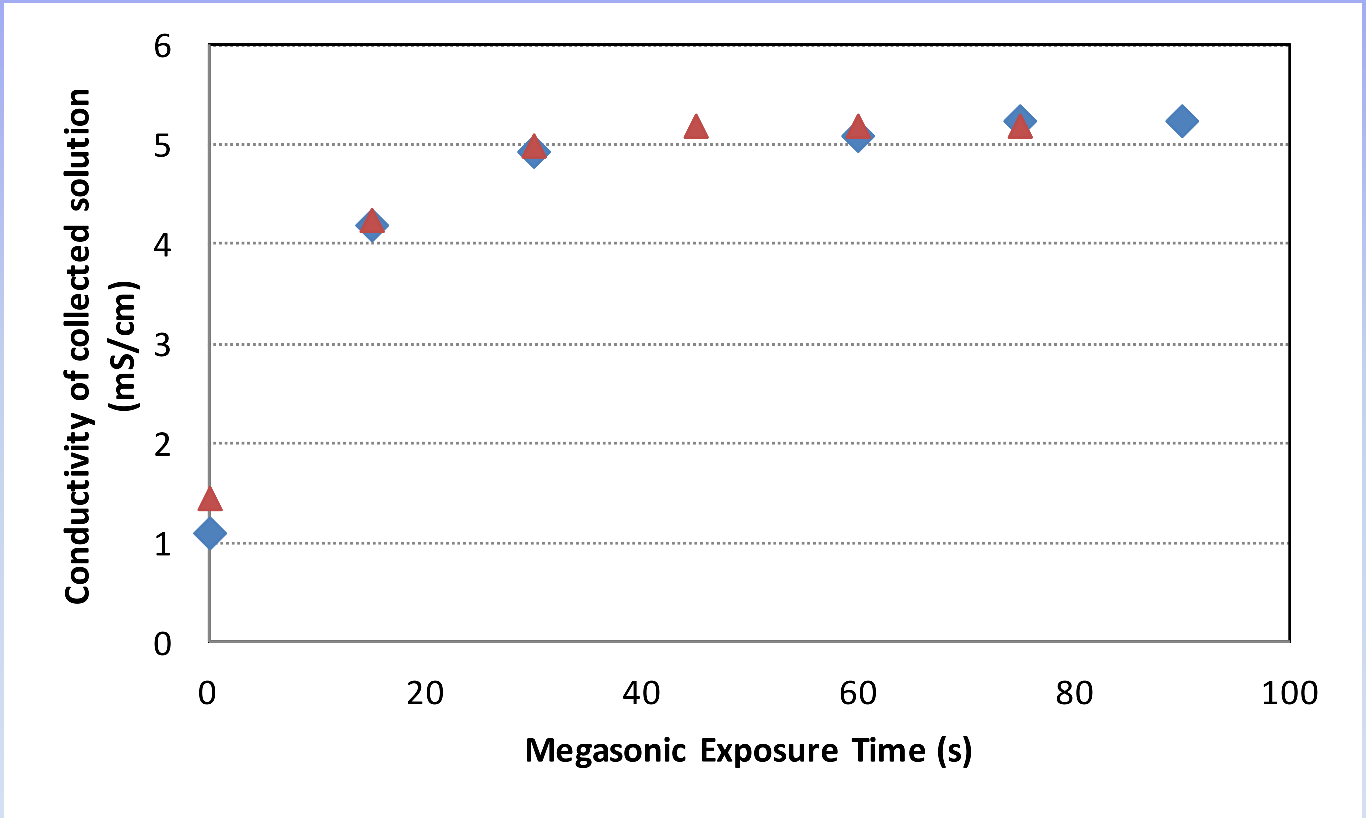
Concentration of OH• increases with meg exposure time

Residence time effect?

- **Hydroxyl radical concentration decreases with increase in NH_4OH conc.**
- **Concentration of OH• similar to that generated in immersion meg system**

Investigation of Residence Time using an Electrolyte (KCl)

- Dispense water (conductivity ~ 1 µS/cm) at 300 ml/min on 8” Si water rotating at 30 rpm
- Replace water by KCl solution of conductivity ~ 5.3 mS/cm and start meg
- Collect samples from effluent stream and analyze for conductivity



- **Almost similar time (~30 s) for KCl to replace DI water as the time for reaching constant OH• conc. during meg exposure (previous slide)**

Summary

- **Generation rate of $OH^{\bullet} \downarrow$ with NH_4OH concentration**

- **In aqueous NH_4OH solutions saturated with various dissolved gases, generation rate of $OH^{\bullet}$ decreases in the following order: $Ar > Air > CO_2$**

- **At pH ~11.2, generation rate of $OH^{\bullet}$ depends on type of alkali used**

- **Generation of $OH^{\bullet}$ concentration was very similar in immersion and single wafer megasonic systems suggesting that single wafer meg tool is as effective as immersion meg tool**