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Measurement of hydroxyl radicals in wafer cleaning solutions irradiated with megasonic waves ☆

M. Keswani [a,*], S. Raghavan [a], R. Govindarajan [a], I. Brown [b]

[a] Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA
[b] Tokyo Electron Limited, Austin, TX 78741, USA

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ABSTRACT

Megasonic irradiation of aqueous solutions produces hydroxyl radicals primarily from dissociation of water under extreme transient cavitation temperature conditions. In the current study, the effect of various sound field (~1 MHz) and solution parameters on rate of generation of hydroxyl radicals in alkaline cleaning solutions of interest to semiconductor industry has been investigated. These parameters include transducer power density, liquid temperature, nature of dissolved gases, solution pH, and type of alkali. Terephthalic acid based fluorescence spectroscopy technique is used for the measurement of concentration of hydroxyl radicals.

1. Introduction

Megasonic irradiation of liquids is known to enhance removal of particulate contaminants from surfaces [1,2]. The two common mechanisms that are believed to assist in particle removal include acoustic cavitation and streaming [3]. Acoustic streaming refers to time independent motion of liquid due to viscous attenuation and can be classified into Eckart, Rayleigh, or Schlichting streaming depending on the length scale of flow vortices that are formed [4–6]. In acoustic cavitation, bubbles are formed during the rarefaction cycle of the sound wave. Some of these bubbles oscillate for several cycles while others grow in size by rectified diffusion and eventually collapse in less than a few cycles. The continuously oscillating bubbles are referred to as stable bubbles whereas collapsing bubbles are called transient bubbles. During collapse of transient bubbles, their inside could reach temperatures of a few thousand degrees, depending on the acoustic field conditions and solution parameters. Under such extreme temperature conditions, different types of radicals such as hydroxyl radicals ($OH^{\cdot}$) are formed in aqueous solutions from thermal dissociation of water molecule [7]. The hydroxyl radicals, with high standard reduction potential of 2.8 V, can cause etching of metals during megasonic cleaning and may also aid in stripping of photoresists [8].

Common techniques that have been used to characterize the intensity of transient cavitation include sonoluminescence, potassium iodide dosimetry, electron spin resonance spectroscopy, Fricke dosimetry and fluorescence spectrometry [9,10]. The formation of hydroxyl and hydrogen radicals in megasonic (~1.6 MHz and 50 W/cm^2) irradiated aqueous solutions of neutral pH saturated with different dissolved gases such as O_2, N_2, Ar, Ne, He, and H_2 at 25 °C was investigated by Kohno et al. [11]. Using electron spin resonance (ESR) technique with 5,5 dimethyl-1-pyrroline N oxide (DMPO) as a probe, the concentration of radicals was measured as a function of time. Only $OH^{\bullet}$ and $H^{\bullet}$ were detected in O_2 and H_2 saturated water, respectively. The concentrations of $OH^{\cdot}$ and $H^{\cdot}$, measured in the range of 0–50 μM, were linear in the first 30 s of irradiation and increased in the order $O_2 > N_2 > Ar > Ne > He$ for $OH^{\cdot}$ while that for $H^{\cdot}$ increased in the order $Ar > Ne > N_2 > He > H_2$. Increasing the bulk solution temperature of Ar and N_2 saturated aqueous solutions from 10 to 50 °C increased the concentration of $OH^{\cdot}$ and decreased that of $H^{\cdot}$ by a factor of two.

In the case of gas saturated solutions, the maximum transient cavitation temperature depends on the polytropic index (the ratio of specific heat at constant pressure to that at constant volume) of the gas dissolved in the liquid subjected to megasonic field [12]. This correlation is given by Eq. (1), where T_{max} is the maximum temperature inside the bubble at the end of its collapse, γ is the polytropic index of the gas dissolved in the liquid, P_m is the liquid pressure equal to sum of atmospheric pressure and pressure amplitude of the sound wave, T_0 and P_i are the temperature and

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* Corresponding author. Tel.: +1 (520)270 4361; fax: +1 (520)621 8059.
E-mail address: manishk@email.arizona.edu (M. Keswani).

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pressure inside the bubble when the bubble is at its maximum size just prior to the collapse. The effect of polytropic index on sonoluminescence intensities from DI water saturated with different gases (air, N_2, O_2, Ar and CO_2) was recently reported by Sangita et al. [13].

$$T_{max} \approx T_0[P_m(\gamma - 1)/P_i] \quad (1)$$

The suitability of terephathalic acid (THA) as a dosimeter for the measurement of concentration of hydroxyl radicals generated in biologically relevant reactions was examined by Barreto et al. [14]. Hydroxyl radicals were generated in aqueous solutions of pH 7.5 containing a phosphate buffer and terephtahlic acid by three different methods, namely (i) irradiation of solution with ultraviolet light at 254 nm, (ii) gamma irradiation with 4000 rads from a cesium source, and (iii) Fenton's type reaction (hydrogen peroxide and copper sulfate). The study concluded that THA was a highly sensitive and specific probe allowing easy detection of 100 nM of OH· concentration. In another study, threshold and extent of cavitation generated using a probe type sonication device (1.1 and 3.3 MHz) was determined through measurement of generation of OH· in air saturated aqueous phosphate buffer solutions of pH 7.0 [15]. Fluorescence spectroscopy employing terephtahlic acid was used. The production of hydroxyl radicals was an order of magnitude lower at higher frequency for constant transducer power density. For example, the OH· concentration increased from 0 to 18 μM after 90 min of megasonic irradiation at 1.1 MHz whereas it only increased to ~1.2 μM for 3.3 MHz for same power density (2.5 W/cm^2). The threshold power density for production of OH· was determined to be 0.5 W/cm^2 and 1.5 W/cm^2 at 1.1 and 3.3 MHz respectively.

The generation of hydroxyl radicals in ultrasonically irradiated phosphate buffer solutions of pH 7.4 was measured using terephthalic acid based fluorescence spectrometry by Mason et al. [16]. Aqueous solutions at 30 °C were subjected to acoustic field at 38 kHz using a cleaning bath type set up and at 20, 40 and 60 kHz using a sonic probe for acoustic powers in the range of 11–50 W. The fluorescence yield, defined as fluorescence intensity divided by the sonic power, varied as 1:2:4 for 20, 40 and 60 kHz indicating that 60 kHz was the best frequency amongst the three for producing maximum concentration of OH·. An inverse correlation was observed between fluorescence intensity and bulk liquid temperature (30 and 90 °C) at 20 kHz frequency and the effect was attributed to increase in vapor pressure with bulk temperature that reduces the cavitation intensity. In a more recent study, the effect of sound intensity (0–2 W/cm^2), duty factor (20–100%) and sonication time (0–60 min) on production of hydroxyl radicals in DI water irradiated with ~1 MHz sound field was investigated using KI dosimetry and terephthalic acid dosimetry methods [17]. A good correlation was observed between iodide dosimetry and terephthalic acid dosimetry both in continuous and pulsating modes at different sound intensities and duty cycles. The KI dosimetry was not sensitive for detection of hydroxyl radicals produced at power densities below ~1 W/cm^2 while terephthalic acid dosimetry was sensitive even at the lowest investigated power density of 0.5 W/cm^2.

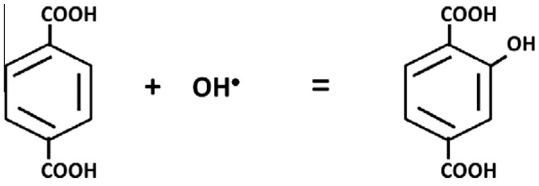
It may be apparent from aforementioned studies that most of the previous work on measurement of hydroxyl radical concentration has been conducted in aqueous solutions of *near neutral pH* of interest to medical community. Semiconductor industry uses alkaline solutions to remove particles from wafer surfaces and to the best of the authors' knowledge, there has been no reported systematic study on such solutions. The current study was undertaken to understand the role of various sound field and solution variables such as transducer power density, bulk liquid temperature, nature of dissolved gas, pH, and type of alkali on rate of generation of hydroxyl radicals in alkaline solutions irradiated with sound waves of ~ 1 MHz frequency.

2. Experimental materials and methods

The chemicals, terephthalic acid (98 wt%), 2-hydroxy terephthalic acid (97 wt%), pH 7.2 phosphate buffer, tetramethylammonium hydroxide aqueous solution (25 wt%) and potassium hydroxide (85 wt%) were purchased from Sigma Aldrich. Ammonium hydroxide solution (29 wt%, MB grade) was procured from KMG electronic Chemicals Incorporated. All gases (air, Ar, CO_2) were greater than 99.9% purity and were provided by University of Arizona Cryogenic Facility.

Aqueous alkaline or buffer (25 ml phosphate buffer (0.028 M of potassium di-hydrogen phosphate and 0.041 M of di-sodium hydrogen phosphate) in 1000 ml DI water) solutions containing 75 μM of terephthalic acid and saturated with a gas of interest were prepared at predetermined temperatures between 10 and 45 °C. The concentration of aqueous ammonia solutions used in the experiments are reported in the form of volume ratio *x*:*y* where *x* in the volume of 29% ammonium hydroxide solution and *y* is the volume of DI water. Gas saturation of solutions was carried out by bubbling the gas for 20 min. A gas blanket was maintained on the surface of the liquid during experiments. The oxygen content of Ar and CO_2 saturated solutions was less than 0.2 ppm as measured using a Thermo Scientific Orion Star A113 dissolved oxygen meter. Acoustic exposure of the solutions (400 ml) was carried out in Megbowl®, a megasonic system manufactured by Product Systems Incorporated (Campbell, CA). The Megbowl® is a polypropylene cylindrical tank (8.9 cm in diameter as well as in length) fitted with a circular transducer (5 cm in diameter, ~1 MHz frequency) at the bottom. After megasonic exposure at power densities between 0.1 and 2 W/cm^2 (continuous mode) for 0.5, 1, 2 and 3 min, samples in the amount of 3 ml were drawn and analyzed for fluorescence intensity. A minimum of two measurements were conducted for each experimental condition in this study.

Fluoroscence measurements were performed using an excitation wavelength of 318 nm and an emission wavelength of 425 nm using Shimadzu RF-5301PC spectrofluorophotometer. The principle of fluorescence spectroscopy is based on capture of hydroxyl radicals by terephthalic acid to form 2-hydroxyterephthalic acid according to reaction 1.



(R1)

For calibration, aqueous solutions of 2-hydroxyterephthalic acid at known concentrations between 0.01 and 2.5 μM were prepared. All fluorescence measurements were done at ~ 25 °C.

3. Results and discussion

Fig. 1 shows the calibration curve (fluorescence intensity vs concentration) for 2-hydroxy terephthalic acid in the concentration range of 0.01–2.5 μM for three different air saturated aqueous solutions with pH values of 7.2, 10.0 and 11.2. The solution pH of 7.2 was achieved by adding phosphate buffer to aqueous solution of hydroxyl terephthalic acid while pH 10.0 and 11.2 were obtained using ammonium hydroxide. At pH 7.2, where most of the data points were obtained, it can be seen that the fluorescence intensity increases linearly with concentration of hydroxyterephthalic acid solution. The lowest concentration of hydroxytereph-