Optimization of Dilute Ammonia-Peroxide Mixture (APM) for High Volume Manufacturing Through Surface Chemical Investigations (Intel Customized Project)

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Cost Share (other than core ERC funding):

- Horiba SC-1 monitor on loan

Objectives

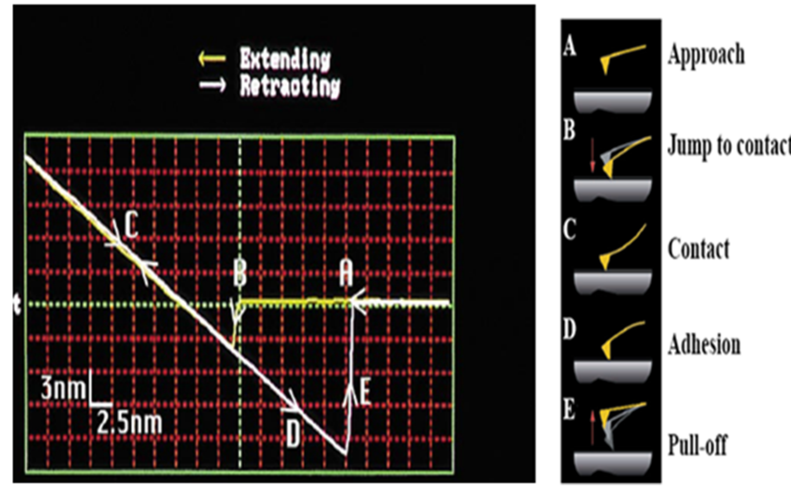
1) Optimization of ammonia-peroxide mixtures (APM) for particle removal through interaction force measurements using atomic force microscope (AFM).

2) Investigation of the stability of ammonium hydroxide and hydrogen peroxide in APM solutions as a function of temperature and Fe^{2+} ion concentrations.

Experimental Approach

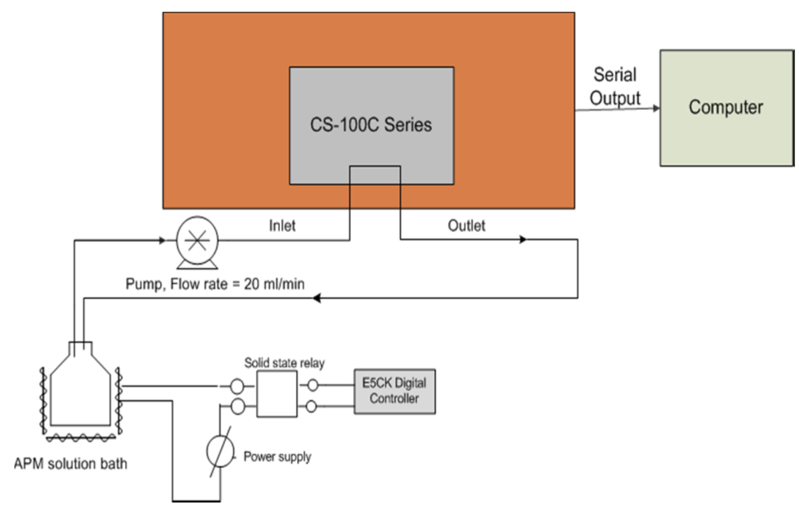
1) Interaction ***(adhesion or repulsive)*** forces measured using atomic force microscope (AFM).

- p-type Si (100) substrate etched in dilute HF(1:100)
- Silicon tip
  - Spring constant = 0.12 N/m.
  - Etched in dilute HF (1:100)



2) $NH_4OH$and H_2O_2 concentrations were ***simultaneously*** measured using Horiba CS-100C composition monitor.

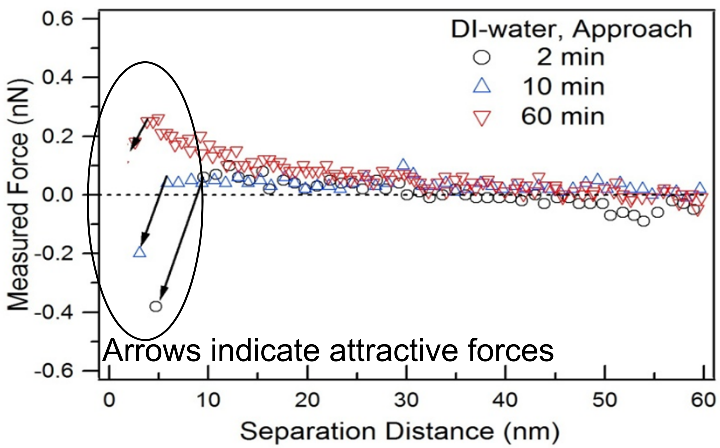
- Solutions: 1:1:5 NH_4OH:H_2O_2:H_2O
- T =24, 40, 50 and 65°C
- Fe^{2+} ion conc. = 0, 5 and 10 ppb
- pH ~ 9.6-10.6

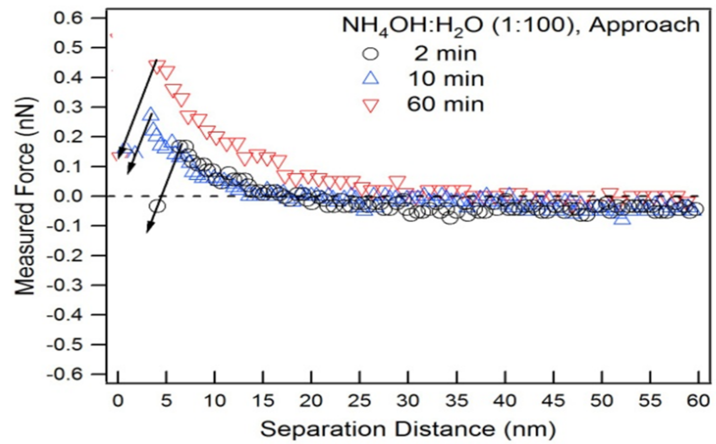


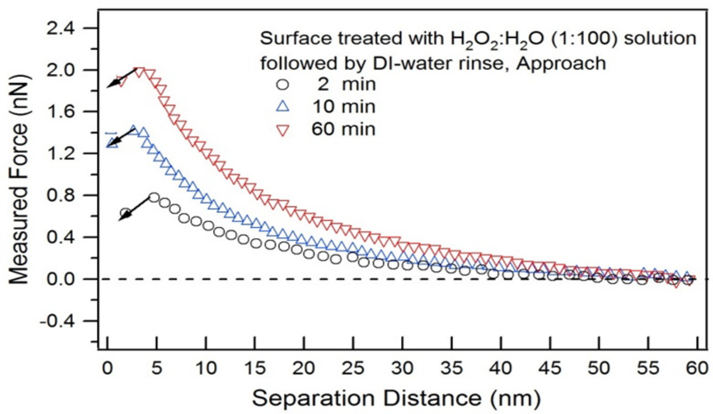
RESULTS I

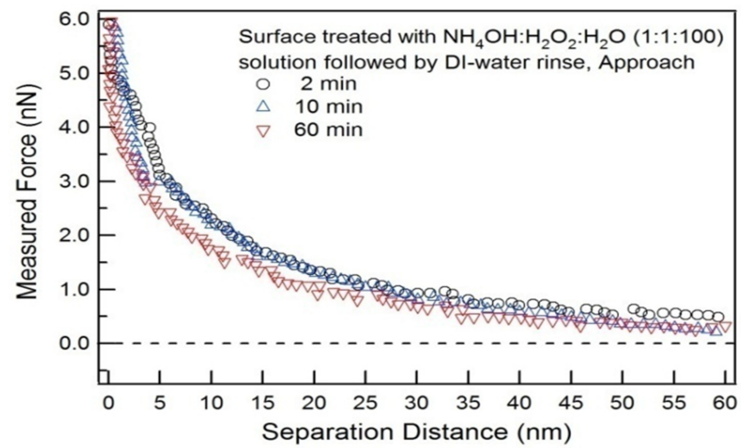
Force measurements between *H-terminated Si surface* and a *H-terminated Si tip* in dilute APM (1:1:100) solution and its components.

Interaction Force Measurements between H-terminated Si surfaces in a dilute APM Solution & its Components





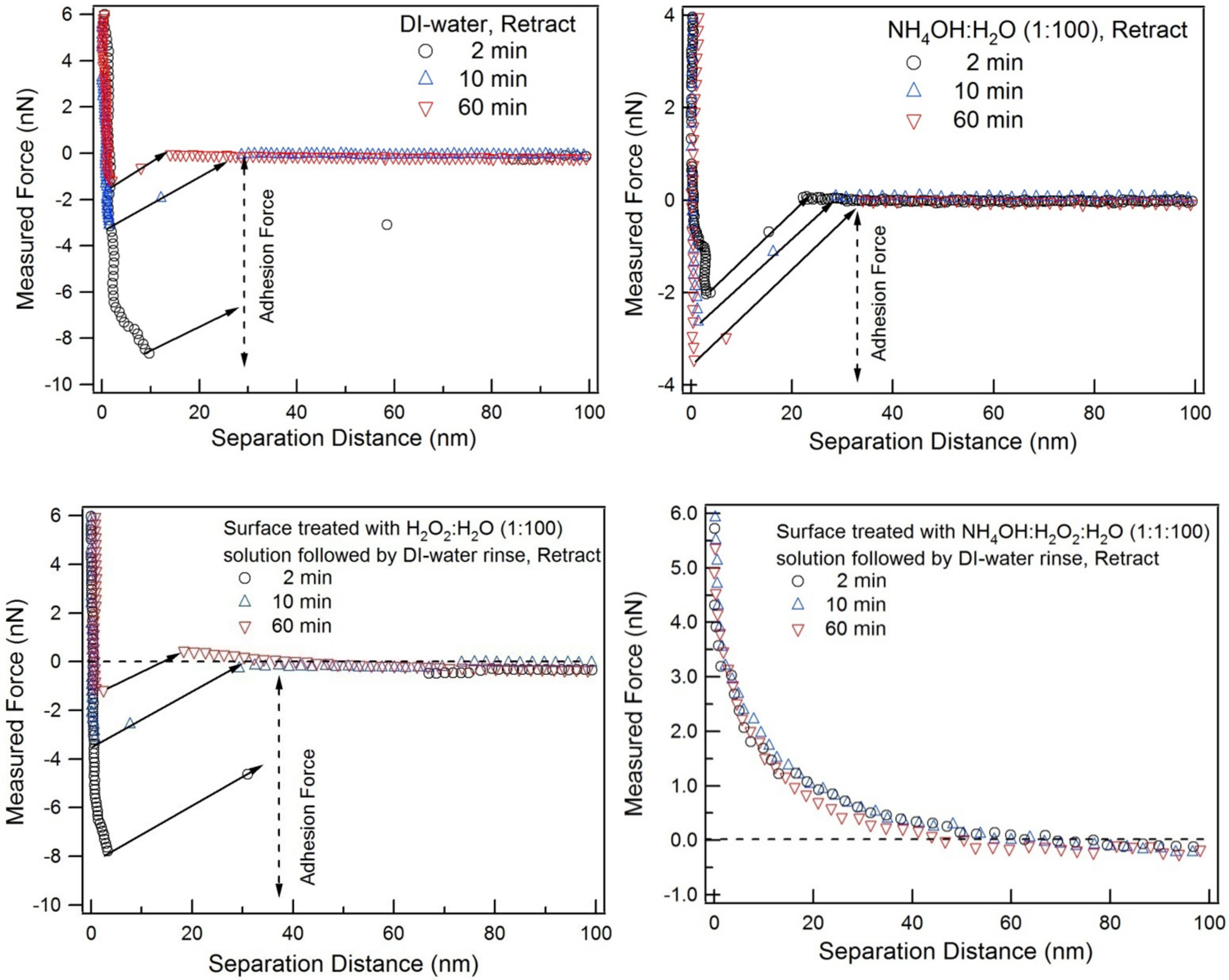




- In DI-water, $NH_4OH:H_2O$ (1:100) and $H_2O_2:H_2O$ (1:100) solutions, repulsive forces were measured at long distances. Attractive forces exist at short separation distances (10 nm)

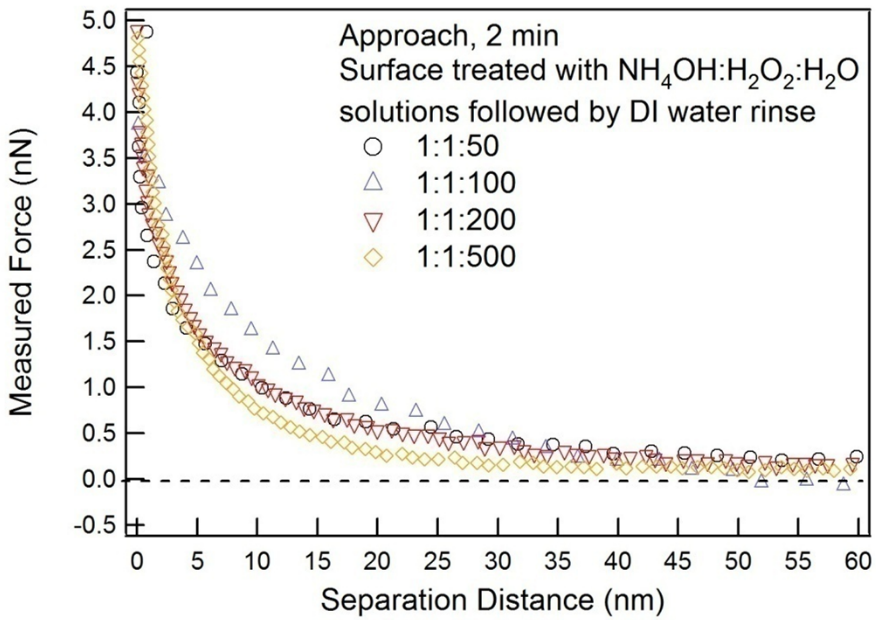
- In a dilute APM (1:1:100) solution, only repulsive force was measured between Si surface and Si tip.

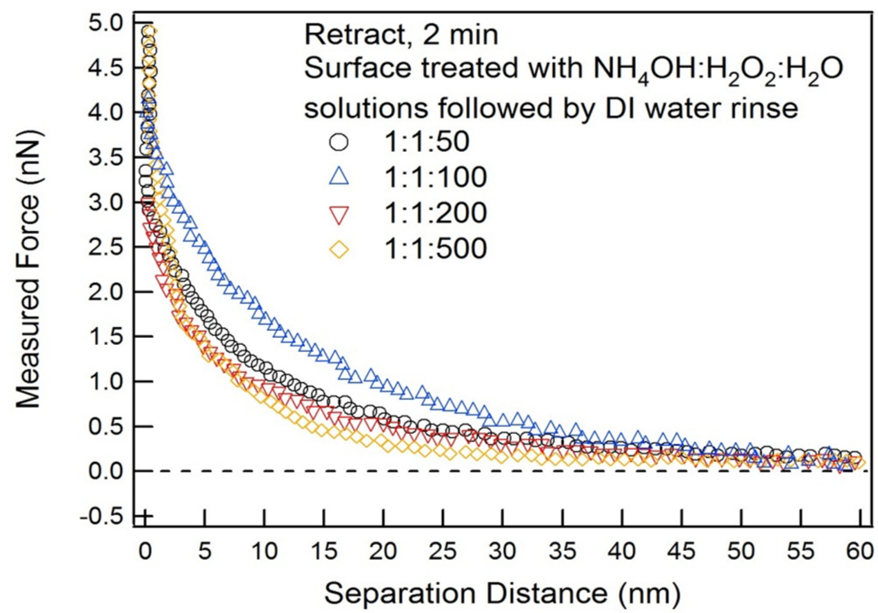
Adhesion Force Measurements between a H-terminated Si surfaces in a dilute APM Solutions & Components



- Adhesion force exists between Si surface and Si tip in DI-water, $NH_4OH:H_2O$ (1:100) and $H_2O_2:H_2O$ (1:100) solutions.
- Adhesion force decreased with an increase in time
- Only repulsive force was measured between Si surface and Si tip in a dilute APM 1:1:100 solution.

Effect of dilution on Interaction forces between H-terminated Si surfaces



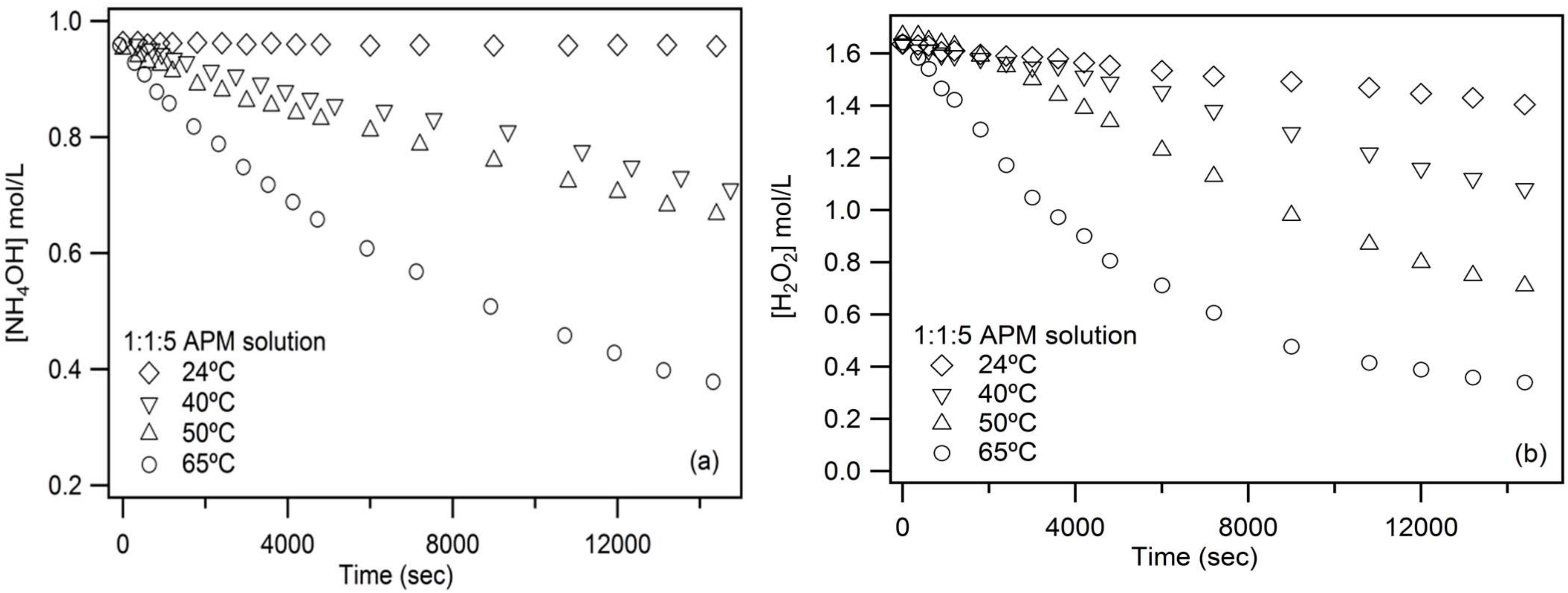


- Both approach and retract curves between Si surface and Si tip show a net repulsive force in APM solutions ranging from 1:1:50 to 1:1:500 within 2 min of immersion.
- *These results indicate that particle re-deposition can be prevented in even very dilute APM solutions*.

RESULTS II

Measurements of the stability of *ammonium hydroxide* and *hydrogen peroxide* in APM solutions using Horiba SC-1 composition monitor.

Decomposition of NH_4OH and H_2O_2 in 1:1:5 APM Solution



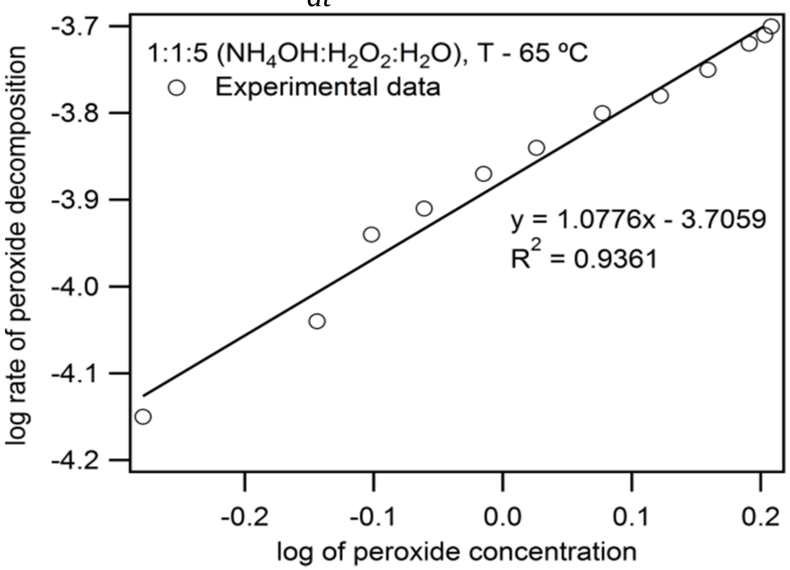
- Ammonia decomposition increases with temperature.
  - In one hour, ammonia concentration decreased by 30% at 65°C .
- Increase in temperature results in higher hydrogen peroxide decomposition.
  - Time for 50% decomposition is roughly 2.8 and 1.0 hr at 50°C and 65°C, respectively.

Kinetic Analysis of H_2O_2 Decomposition without the presence of Fe^{2+} ions in APM Solutions

$$H_2O_2 \leftrightarrow 2H_2O + O_2 \Rightarrow \frac{-d[H_2O_2]}{dt} = k[H_2O_2]^{\alpha}$$

$$\log \frac{-d[H_2O_2]}{dt} = \log k + \alpha \log[H_2O_2]$$

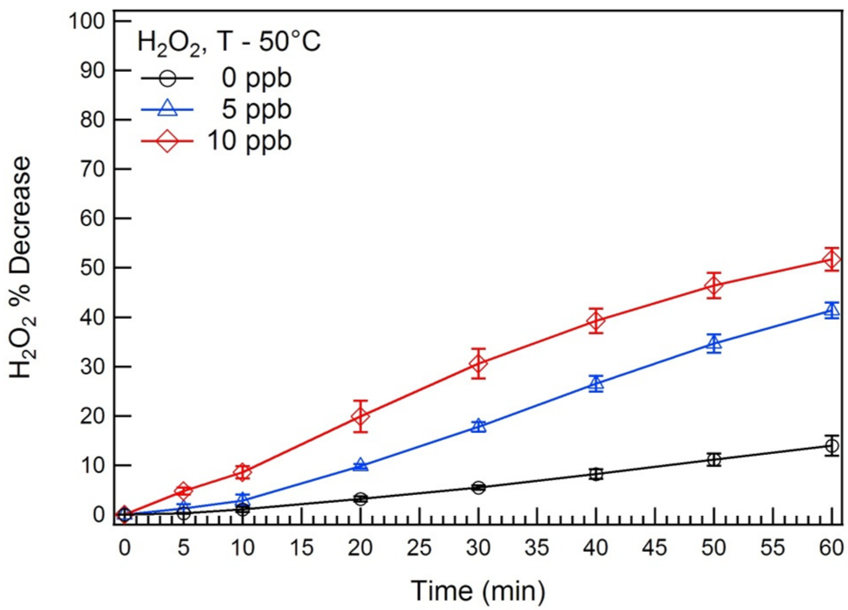
- *$[H_2O_2]$ = peroxide concentration*
- *k* = rate constant
- α = reaction order

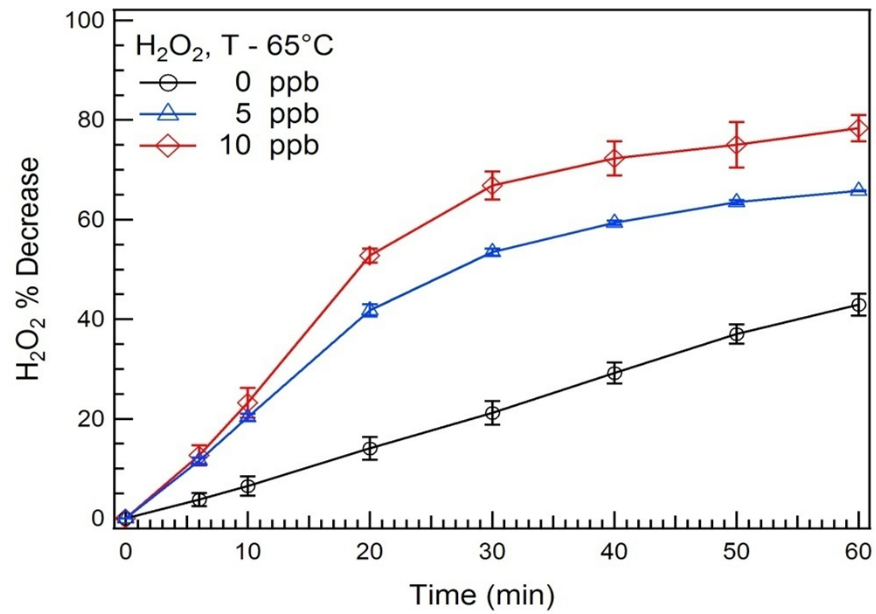


T (°C)	α	k (sec^{-1})
$NH_4OH:H_2O_2:H_2O$ (1:1:5)		
50	0.95 ± 0.10	8.5×10^{-5}
65	1.00 ± 0.04	2.0×10^{-4}

- Peroxide decomposition follows a first-order reaction kinetics with respect to H_2O_2 for 1:1:5 APM Solutions
- Increase in temperature resulted in a higher rate constants for 1:1:5 APM solutions.

Decomposition of H_2O_2 in the presence of Fe^{2+} ions in 1:1:5 APM Solution



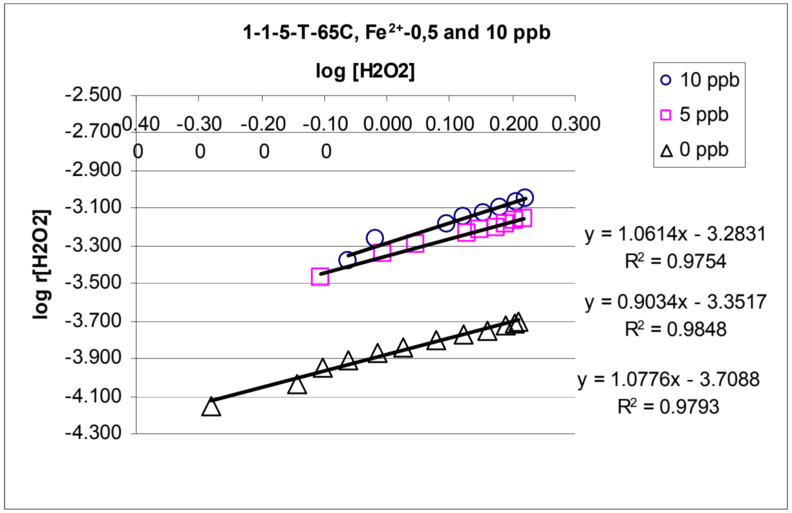


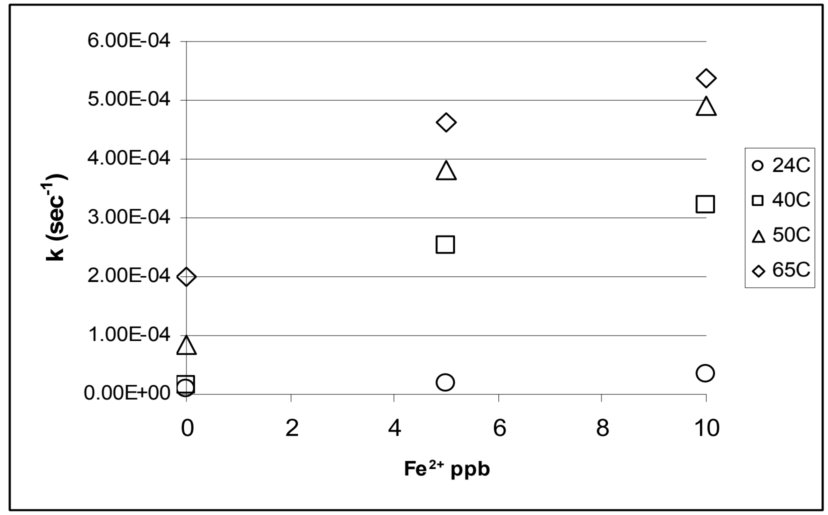
- Hydrogen peroxide decomposition increases with Fe^{2+} concentration and temperature.
- Highest peroxide decomposition was measured in the presence of 10 ppb Fe^{2+} ion at 65°C.
  - Time for 50 % decomposition is roughly 30 and 20 min at 5 and 10 ppb of Fe^{2+}.

Possible H_2O_2 Decomposition Mechanism in the Presence of Fe^{2+} ions in APM Solutions

$$H_2O_2 \leftrightarrow 2H_2O + O_2 \Rightarrow \frac{-d[H_2O_2]}{dt} = k'[H_2O_2]^{\alpha}$$

- $[H_2O_2]$ = peroxide concentration
- $k' = k\,[Fe^{2+}]$
- α = reaction order





- Iron induced peroxide decomposition follows a first-order reaction kinetics with respect to H_2O_2 for 1:1:5
- In the excess of H_2O_2 concentration over $[Fe^{2+}]$, catalytic decomposition follow $H_2O_2 \leftrightarrow 2H_2O + O_2$
  - Reported literature shows H_2O_2 decomposition is a first order reaction kinetics with respect to $[H_2O_2]$
- Calculated rate constant increased with an increase in $[Fe^{2+}]$ and temperature.
- Activation energy of 55 kJ/mol was calculated in the presence of Fe^{2+} containing APM solutions compared to 70 kJ/mol without the presence of Fe^{2+}.
  - Similar rate constants and activation energy are reported in literature.

Key Highlights

- Adhesion forces prevailed between H-terminated Si surface and a H-terminated Si tip in DI water, ammonium hydroxide and hydrogen peroxide solutions up to 60 min.
  - Attractive forces were attributed to van der Waals forces at separation distances of < 10 nm.
- Interaction force measurements in dilute APM (1:1:100) solution showed repulsive forces starting at a separation distance of 60 nm within 2 min of immersion time.
- Ammonium hydroxide and hydrogen peroxide decomposition increases with temperature of APM solutions.
- Hydrogen peroxide decomposition increases with Fe^{2+} concentration
- Peroxide decomposition in APM solutions follows a first-order kinetics with respect to $[H_2O_2]$.

Publications

- S.Siddiqui, J. Zhang, M. Keswani, A. Fuerst, S. Raghavan, “Study of Interaction between Silicon Surfaces in Dilute Ammonia-Peroxide Mixtures (APM) and their Components using Atomic Force Microscope, *Microelectronic Engineering*, In Press *(Available Online)*

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- S.Siddiqui, M. Keswani, R. Biggie, S. Raghavan, “Real-Time Measurements of Ammonium Hydroxide and Hydrogen Peroxide Decomposition in APM Solutions”, In Preparation.

Industrial Interactions

- Avi Fuerst, Intel Corporation
- Barry Brooks, Intel Corporation
- Eric Hebert, Horiba Inc.

Damage Free and Energy Efficient Megasonic Cleaning

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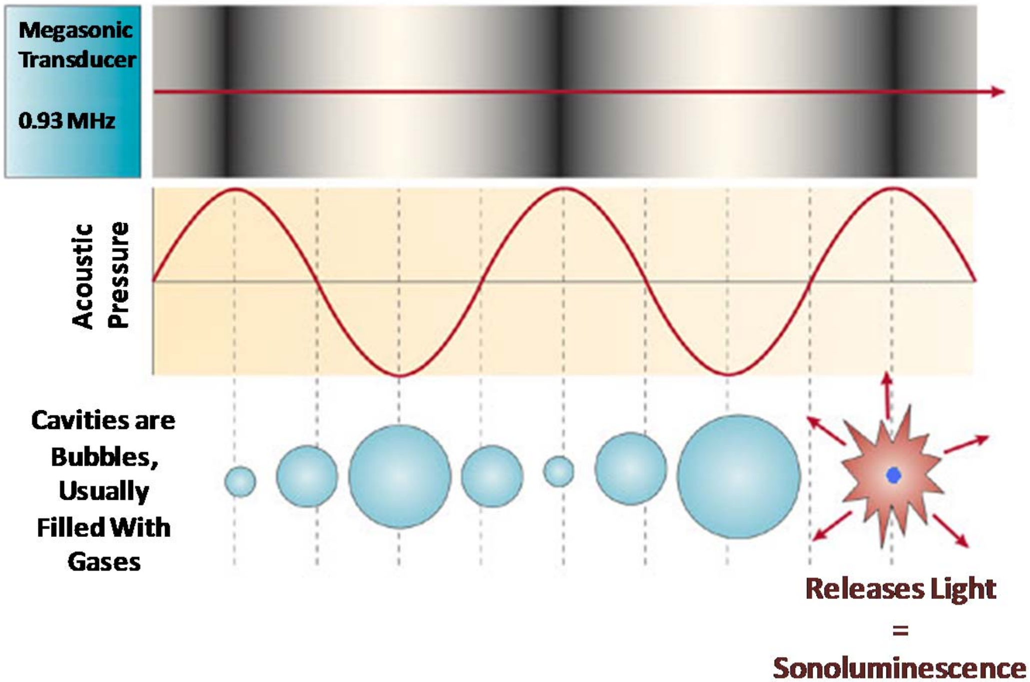
Damage in Megasonic cleaning

- Megasonic cavitation cleans but also damages wafer

- Damage is related to transient cavitation; Control of cavitation has potential application in damage free cleaning

- Sonoluminescence (SL) is a sensitive indicator of cavitation.



Adapted From: Nature Reviews Cancer **5**, 321-327 (2005)

Current Control Strategies for Megasonic Cleaning

- Most commonly used control knobs in Megasonic Cleaning are Applied Power and Chemistry of Cleaning Solutions; frequency of sound field is attracting some attention recently
- Power density in single wafer cleaning tools is typically in the range of 0-3 W/cm^2
- Industry does not make an attempt to optimize **power density** for cleaning based **on the threshold power for onset of cavitation**
- **Type and concentration of dissolved gases, temperature and additives to cleaning solution would affect the cavitation threshold**

Main Objective

❖ **Energy reduction in Megasonic Cleaning Processes through identification and elimination of high energy cavitation events that cause feature damage. This will be done through spectral resolution of Sonoluminescence (SL) data obtained using a novel Cavitation Threshold (CT) Cell**