Steam-Injected SPM Process for All-Wet Stripping of Implanted Photoresist

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Outline

- Motivation
- Implanted PR – All-Wet Stripping Challenge
- SPM (Sulfuric acid – hydrogen Peroxide Mixture) – Making it More Reactive
- Results
- Summary

Low Material Loss – An “All-Wet” Driver

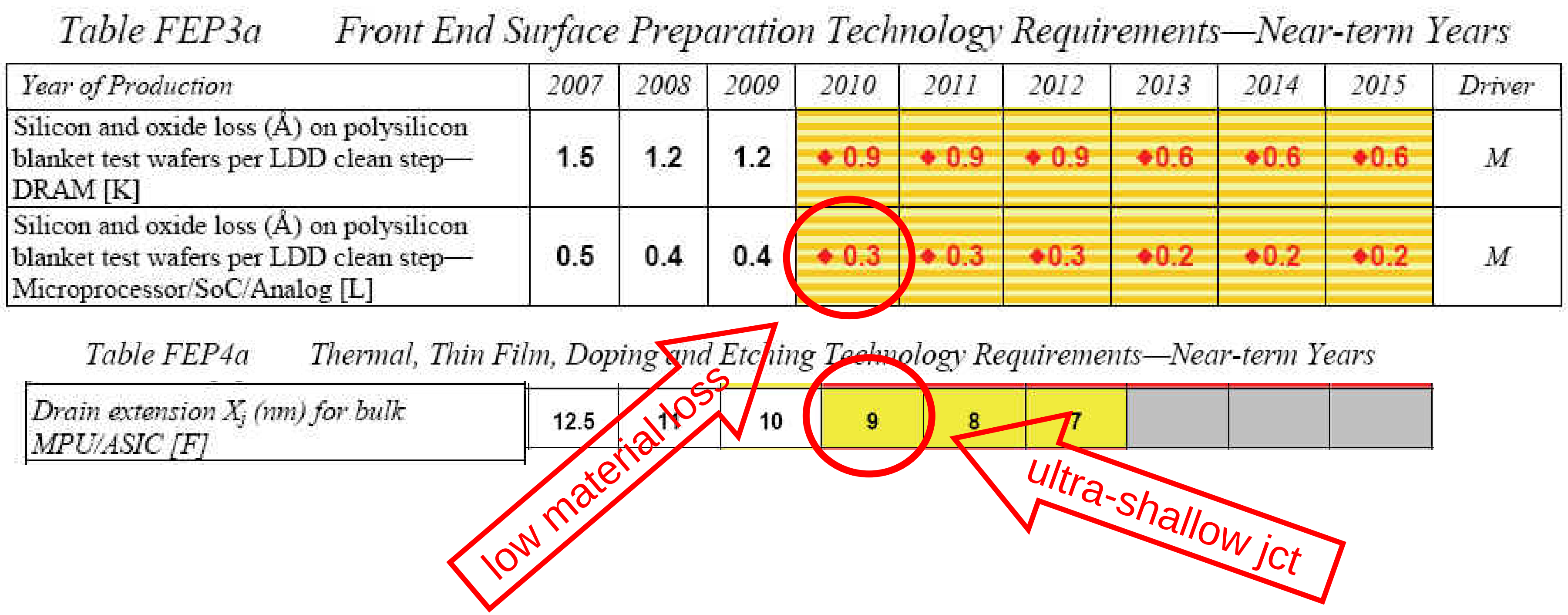


Table FEP3a Front End Surface Preparation Technology Requirements—Near-term Years

Year of Production	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*	*2013*	*2014*	*2015*	*Driver*
Silicon and oxide loss (Å) on polysilicon blanket test wafers per LDD clean step—DRAM [K]	1.5	1.2	1.2	◆0.9	◆0.9	◆0.9	◆0.6	◆0.6	◆0.6	*M*
Silicon and oxide loss (Å) on polysilicon blanket test wafers per LDD clean step—Microprocessor/SoC/Analog [L]	0.5	0.4	0.4	◆0.3	◆0.3	◆0.3	◆0.2	◆0.2	◆0.2	*M*

Table FEP4a Thermal, Thin Film, Doping and Etching Technology Requirements—Near-term Years

Drain extension X_j (nm) for bulk MPU/ASIC [F]	12.5	11	10	9	8	7			

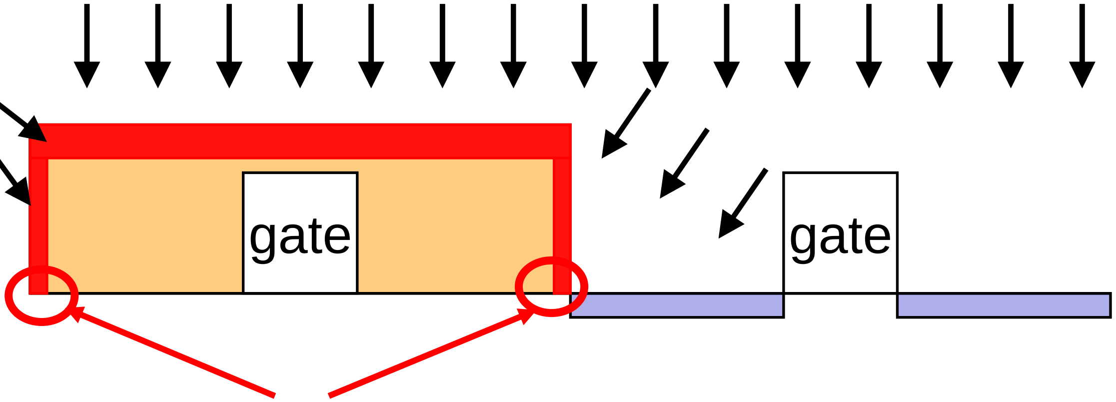
Lower material loss requirements during cleaning driven by ultra-shallow junction (USJ) source-drain extension (SDE) or lightly-doped drain (LDD)

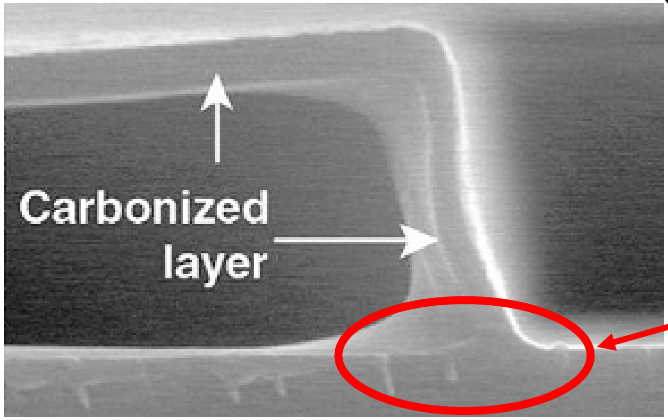
Stripping Implanted Photoresist

Ion implantation process – affects stripping

- Species: B, P, As, Si, Ge, BF_2
- Energy: < 1keV to > 1000keV
- Dosage: $1x10^{11}$ to $>1x10^{16}$ ions/cm^2
- Normal incidence or angled

dehydrogenated, amorphous carbon layer





Most challenging where carbonized PR fused to wafer surface

→ especially at wafer edge, near EBR region

photo source: P. Gillespie et al, *Semiconductor International, October, 1999*

High Activation Energy to Remove Crust

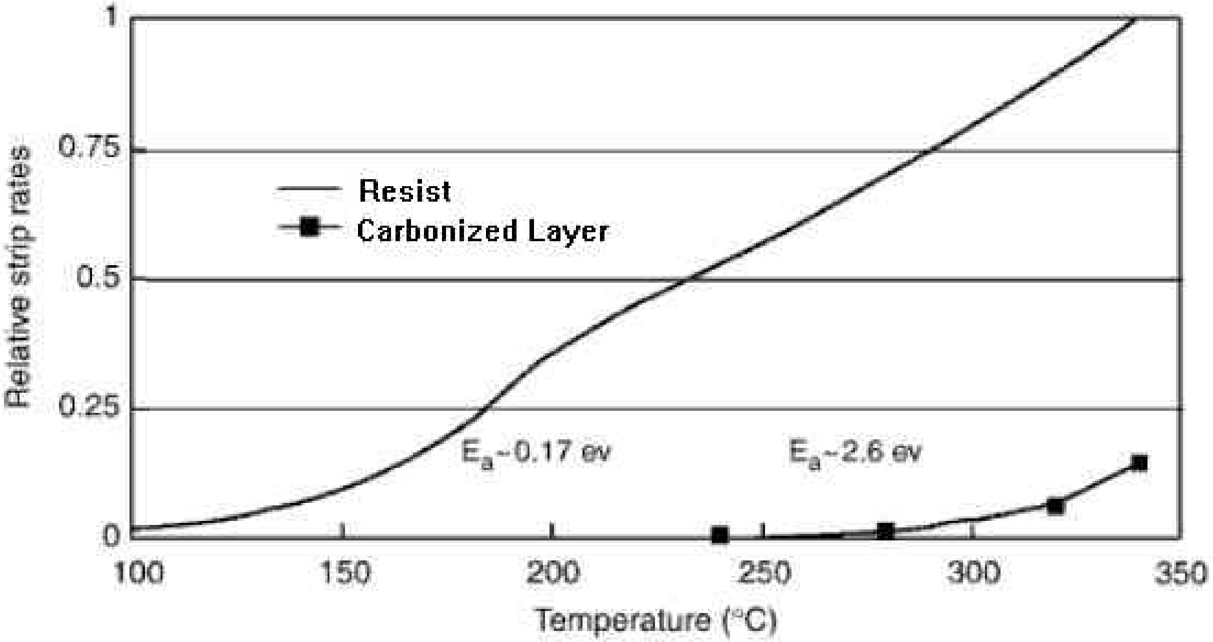
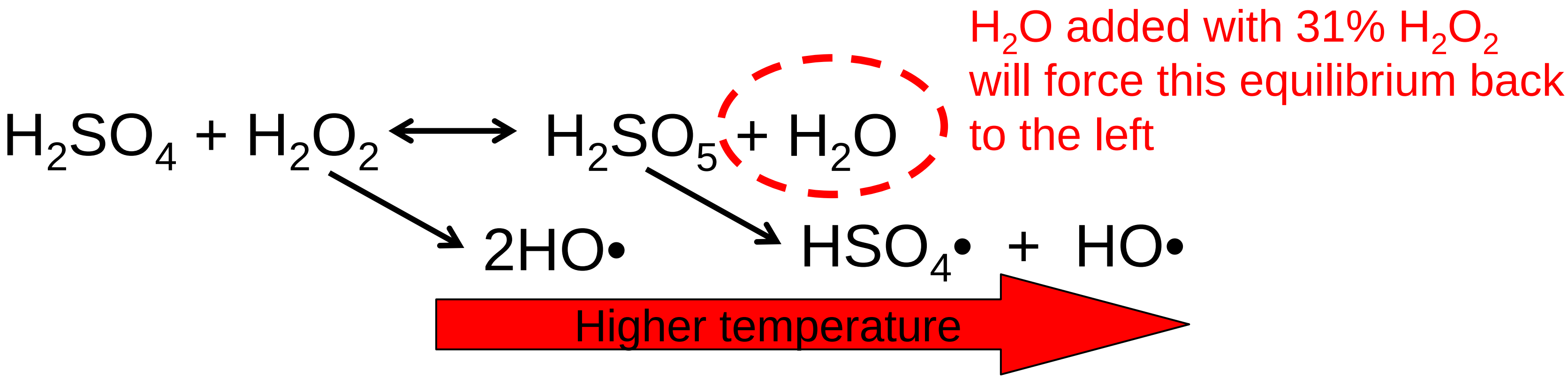


FIGURE 7.57 Relative removal rates of standard i-line photoresist and the implanted carbonized crust layer as a function of temperature for a oxygen plasma without ion bombardment. Activation energy (E_a) has been calculated from the temperature dependence of the reaction.

Robert Doering and Yoshio Nishi, *Handbook of Semiconductor Manufacturing Technology* (CRC Press, 2007).

SPM – Making it More Reactive



$H_2SO_4 + H_2O_2 \longleftrightarrow H_2SO_5 + H_2O$

$2HO\bullet$

$HSO_4\bullet + HO\bullet$

H_2O added with 31% H_2O_2 will force this equilibrium back to the left

Higher temperature

Half Cell Oxidation Reactions

$$HSO_5^- + 2H^+ + 2e^- \longrightarrow HSO_4^- + H_2O \qquad 1.44V$$

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow H_2O \qquad 1.78V$$

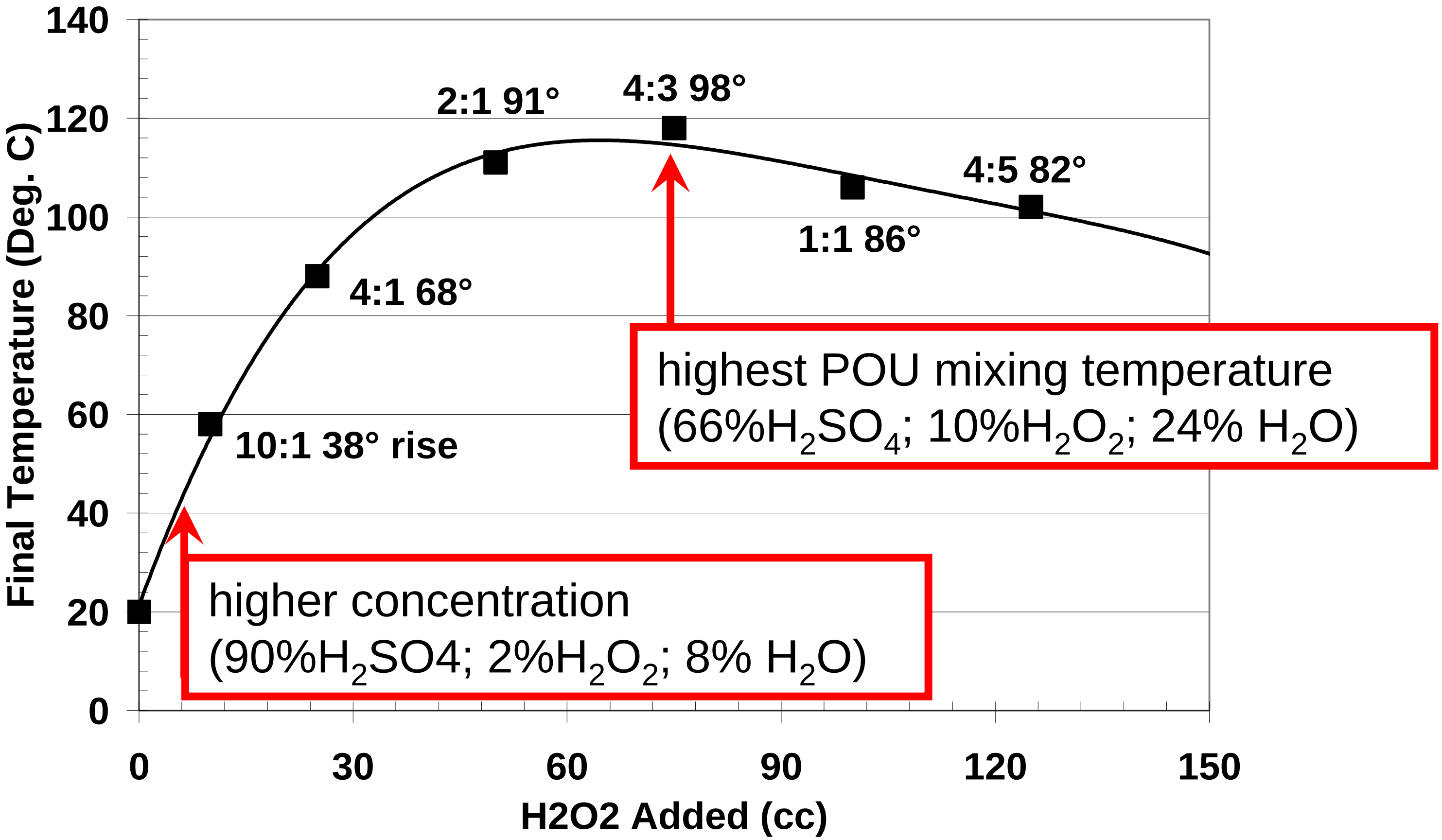
$$HSO_4\bullet + H^+ + e^- \longrightarrow H_2SO_4 \qquad 2.60V$$

$$HO\bullet + H^+ + e^- \longrightarrow H_2O \qquad 2.80V$$

More oxidizing power

SPM Mixing is Exothermic

4:3 ratio gives highest temperature rise, but higher concentration is desired (H_2O_2 includes 69% water, which dilutes and lowers reactivity)



highest POU mixing temperature ($66\% H_2SO_4$; $10\% H_2O_2$; $24\% H_2O$)

higher concentration ($90\% H_2SO4$; $2\% H_2O_2$; $8\% H_2O$)

Resulting temperature when 20° C 31% H_2O_2 is mixed with 100 cc of 20° C 96% H_2SO_4.

How to Achieve High Temperature Without Dilution?

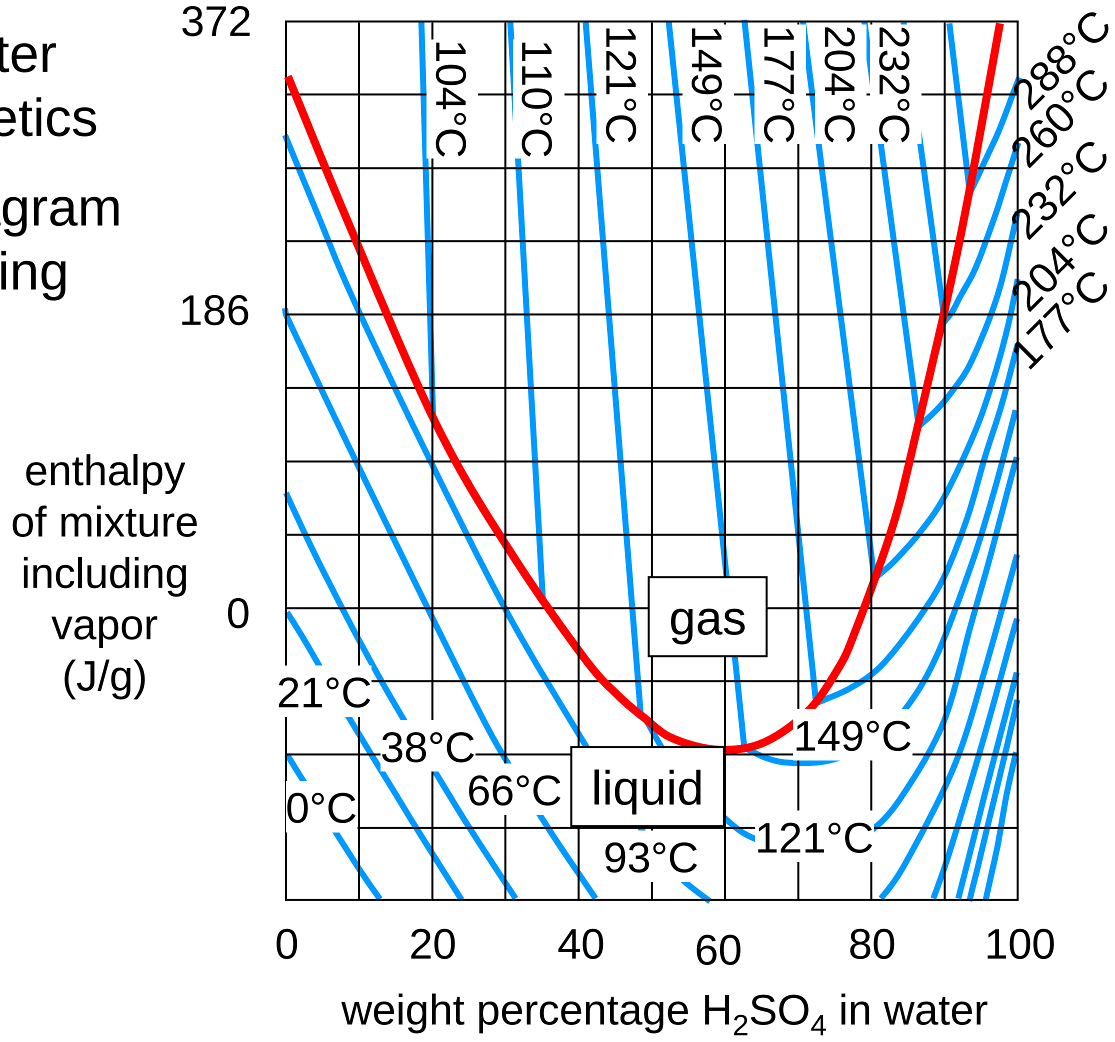
- Pre-heating SPM above 150°C causes rapid degradation of H_2O_2 before contacting the wafer
- POU 4:3 SPM mixing gives temperature boost, but causes dilution
- Preheating H_2SO_4 above 150°C requires specialized fluid handling

→ **SOLUTION = STEAM INJECTION (ViPR+)**

First, lets review a useful tool for illustrating the advantage of steam injection . . . .

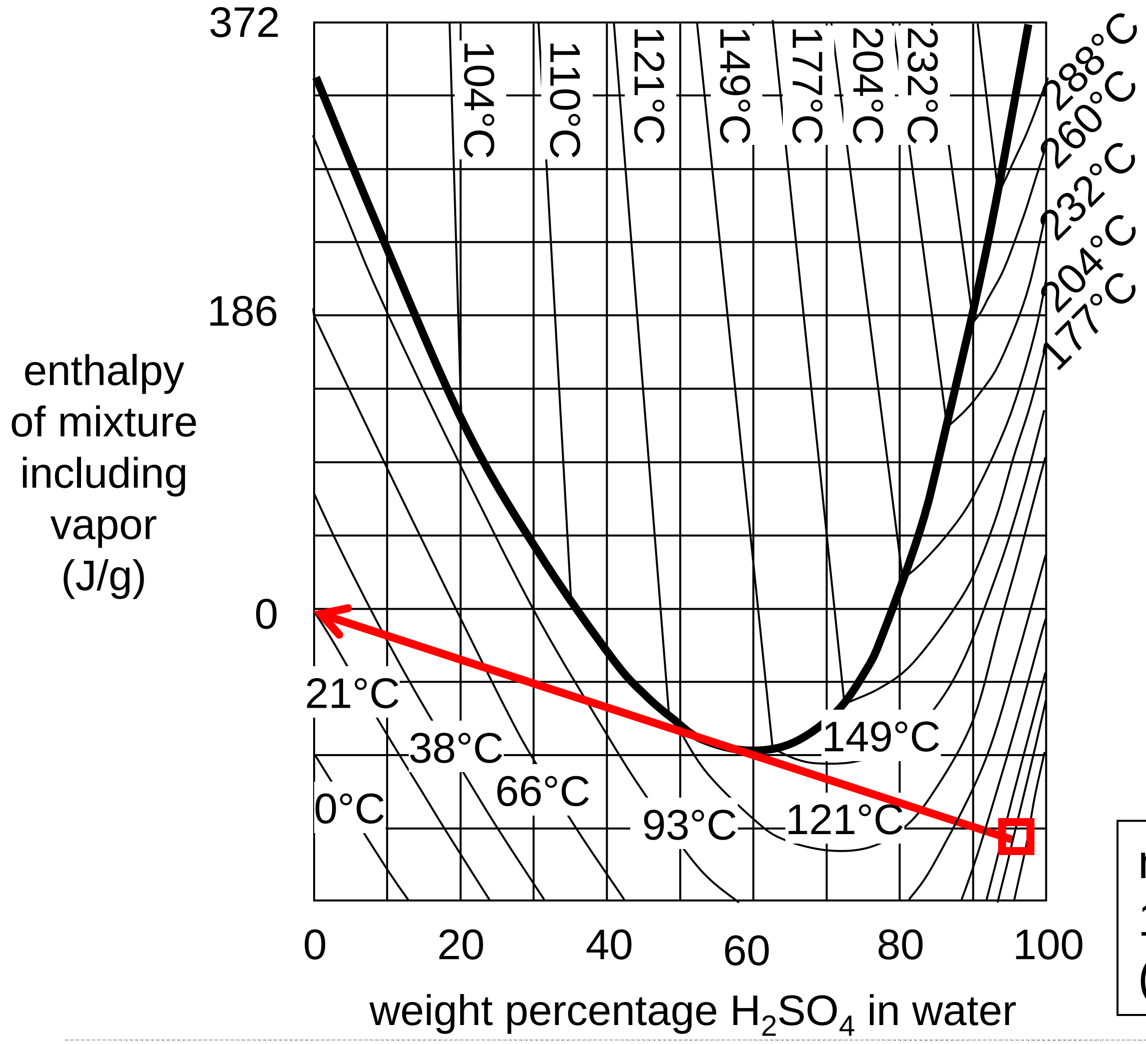
Sulfuric Acid Enthalpy-Concentration Diagram

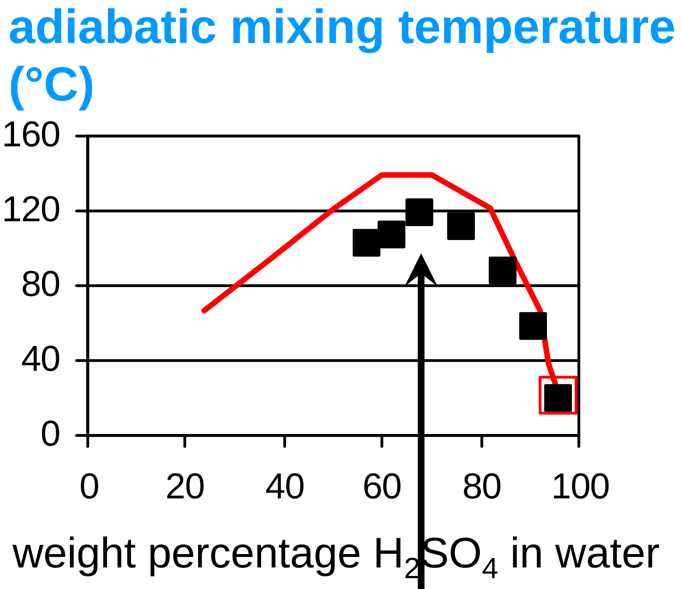
- Mixing sulfuric acid and water produces interesting energetics
- Enthalpy-Concentration diagram allows easy analysis of mixing temperature effects
- gas-liquid equilibrium
- isotherms
- minor differences between 100% H_2O (B.P.=100°C) and 69%H_2O/31%H_2O_2 (B.P.=107°C)



Mixing Room Temperature 96% Sulfuric Acid with Water

Connecting two points produces an adiabatic mixing curve

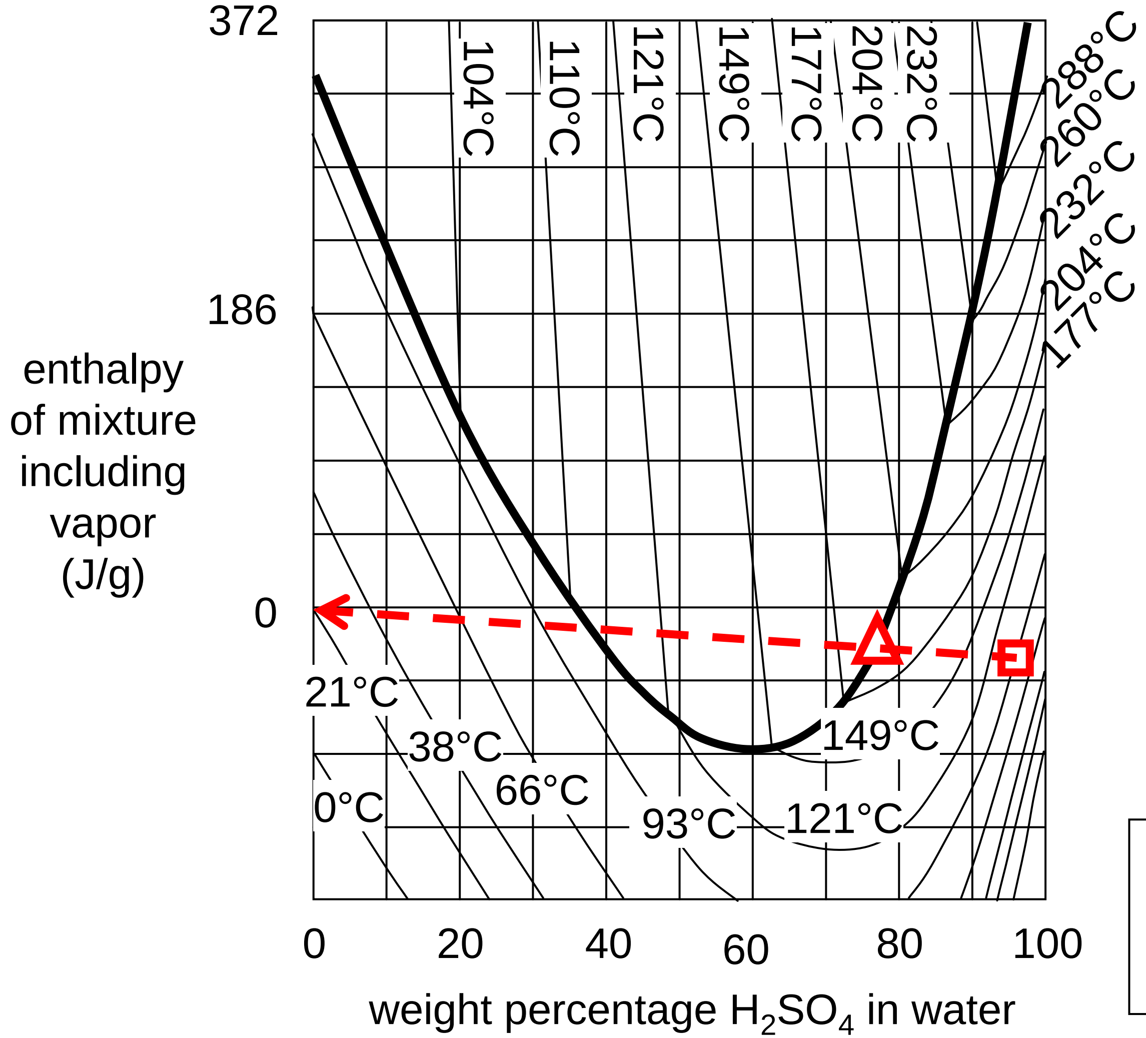


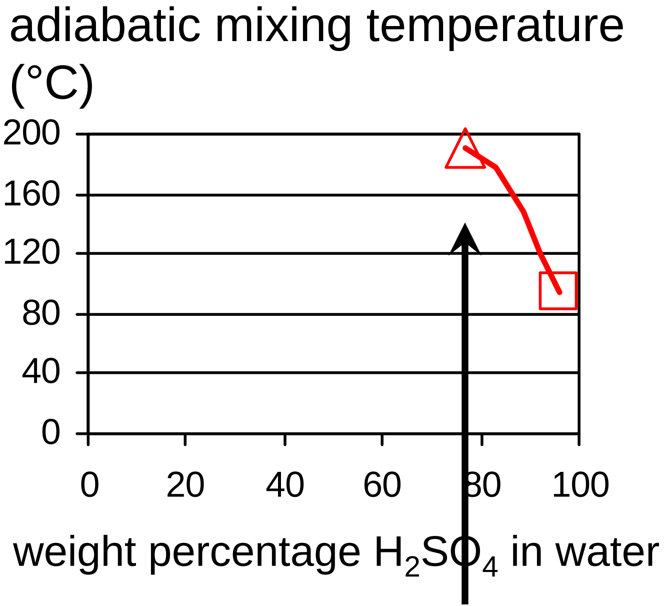


maximum temperature at about 130°C and 4:3 mixing ratio ($66\%H_2SO_4$; $10\%H_2O_2$; $24\%H_2O$)

Mixing 95°C 96% Sulfuric Acid with Water

Starting with 95°C H_2SO_4 causes intersection with gas-liquid curve

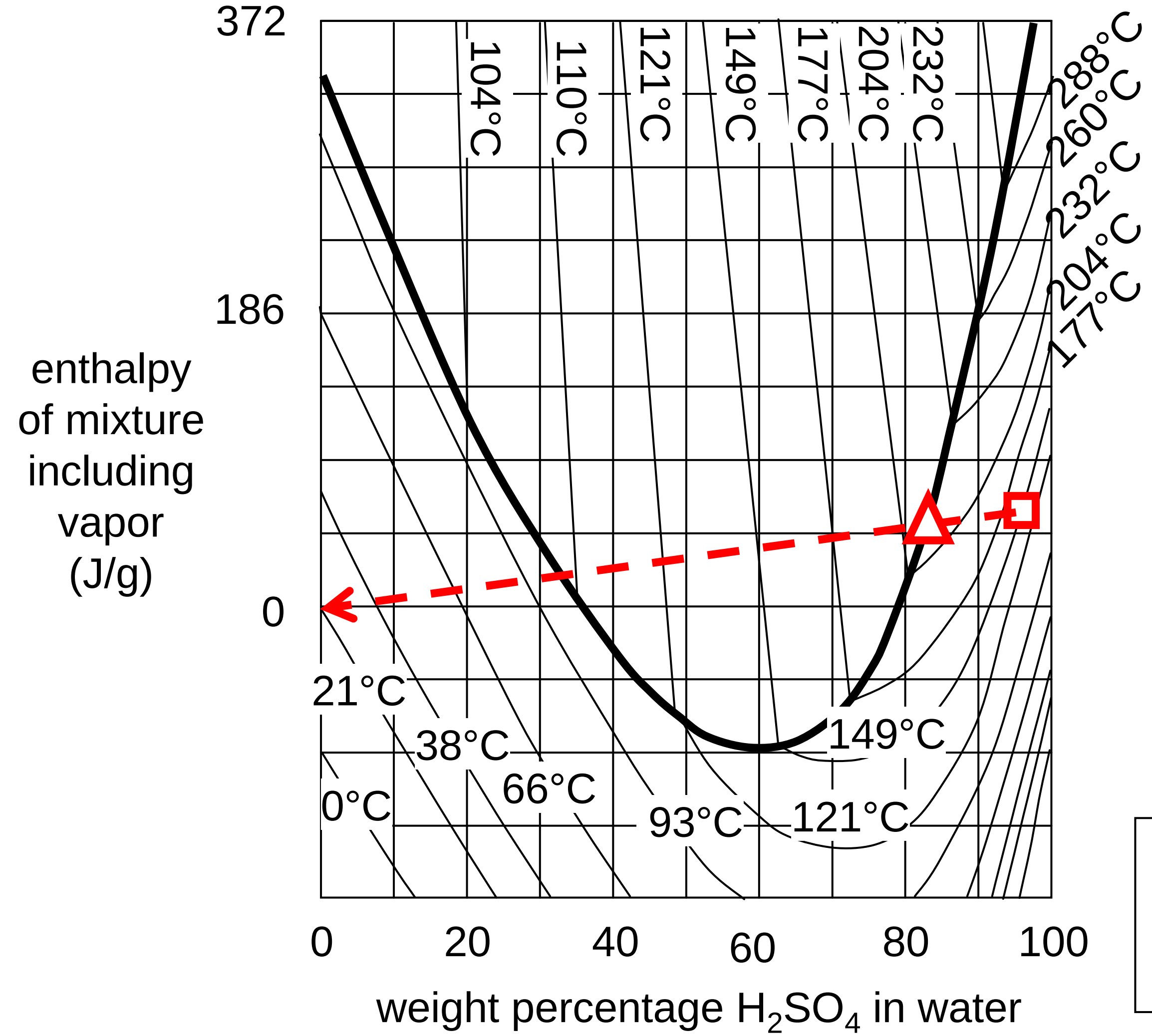


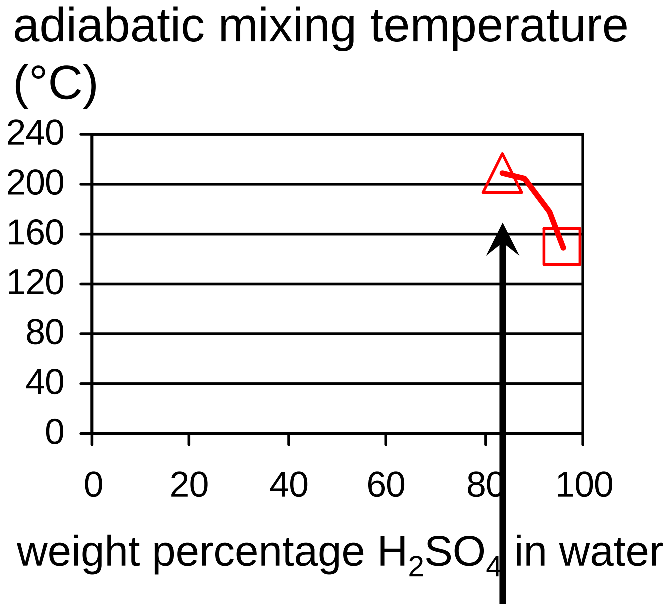

adiabatic mixing temperature (°C)

boiling point at about 190°C and 2.5:1 mixing ratio ($77\%H_2SO_4$; $6\%H_2O_2$;$17\%H_2O$)

Mixing 150°C 96% Sulfuric Acid with Water

Starting with 150°C H_2SO_4 allows 4:1 mixing ratio before boiling

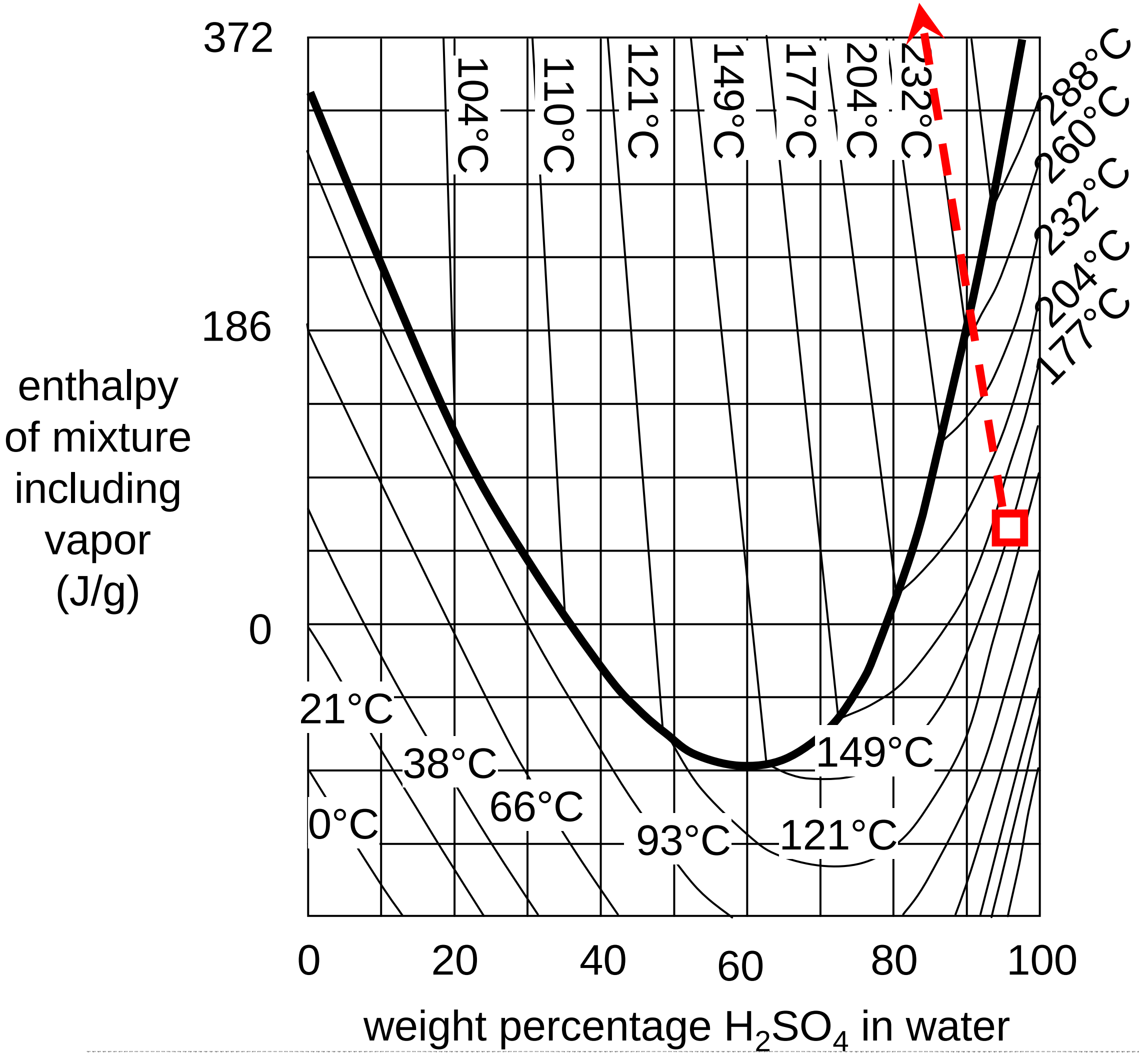




boiling point at about 210°C and a 4:1 mixing ratio ($83\%H_2SO_4$; $4\%H_2O_2$;$13\%H_2O$)

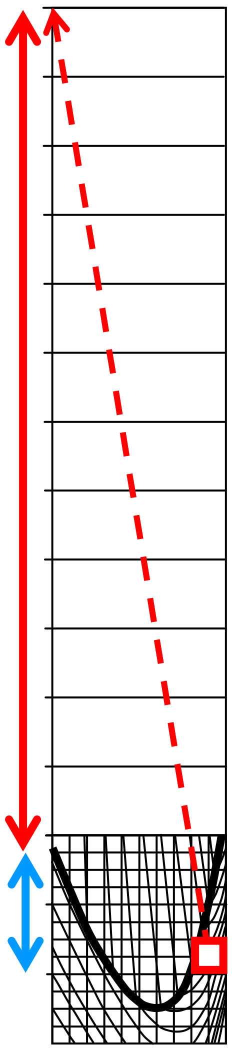
Mixing 150°C 96% Sulfuric Acid with Water and Steam

Heat of Vaporization = The Steam Advantage



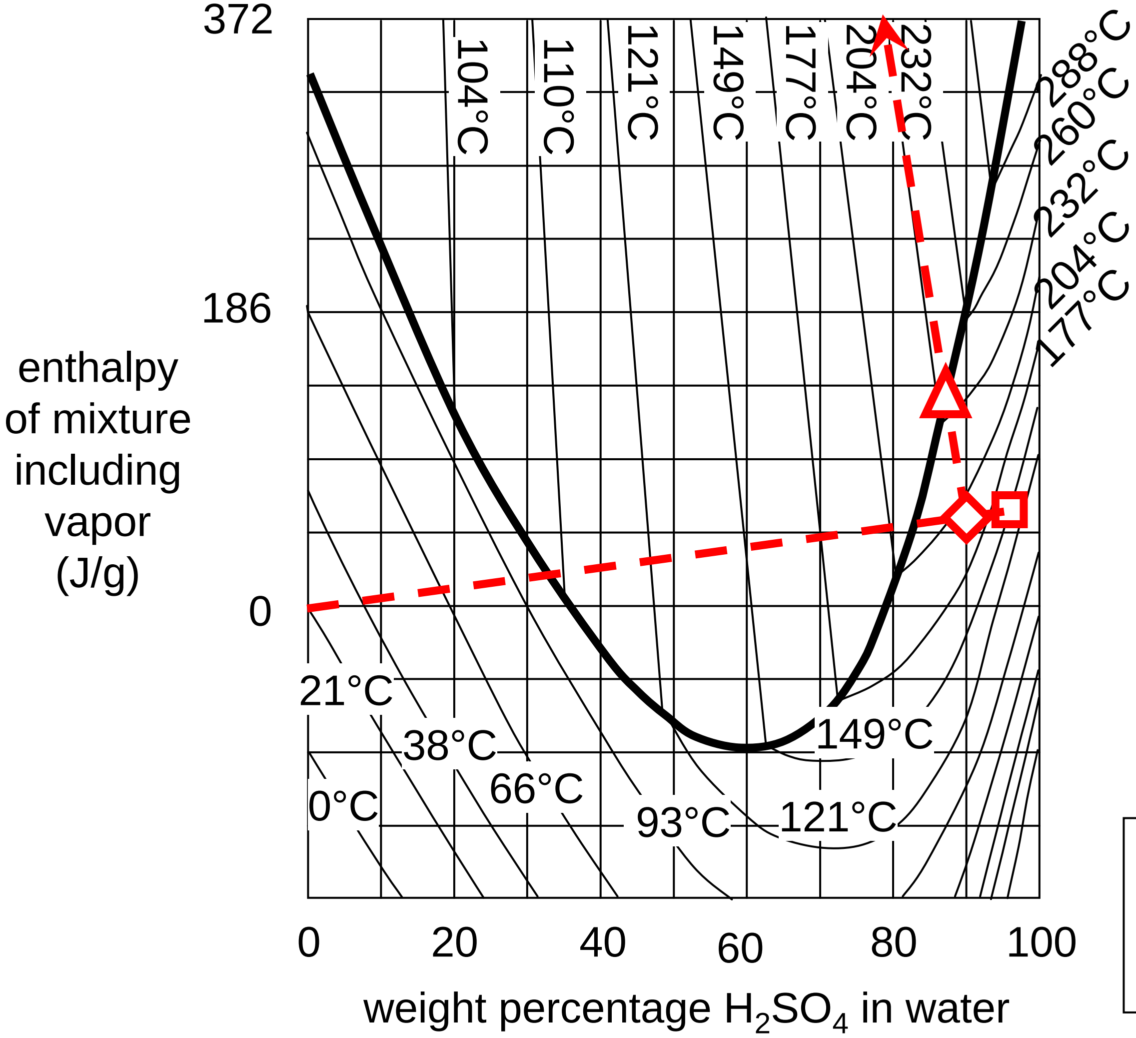
converting water from liquid to gas at 100°C = 2270 J/g

heating water from 21°C to 100°C = 331 J/g

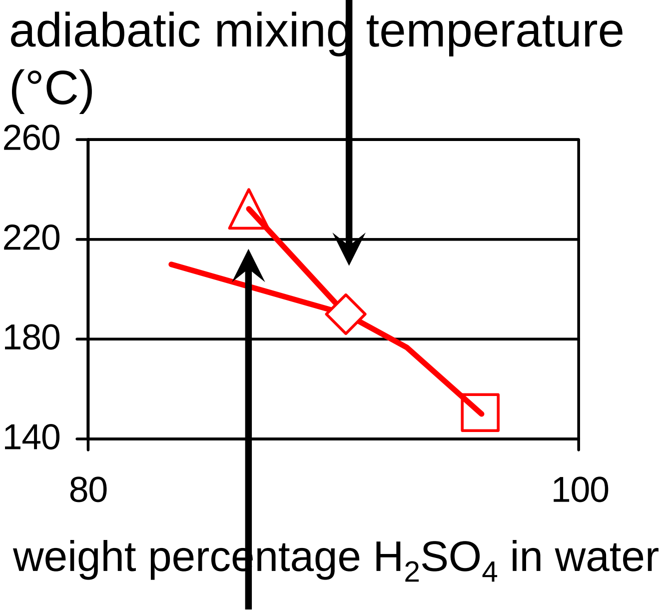


Mixing 150°C 96% Sulfuric Acid with Water and Steam

Using steam provides temperature boost with minimal dilution



add 31% H_2O_2 to reach 10:1 mixing ratio then add steam

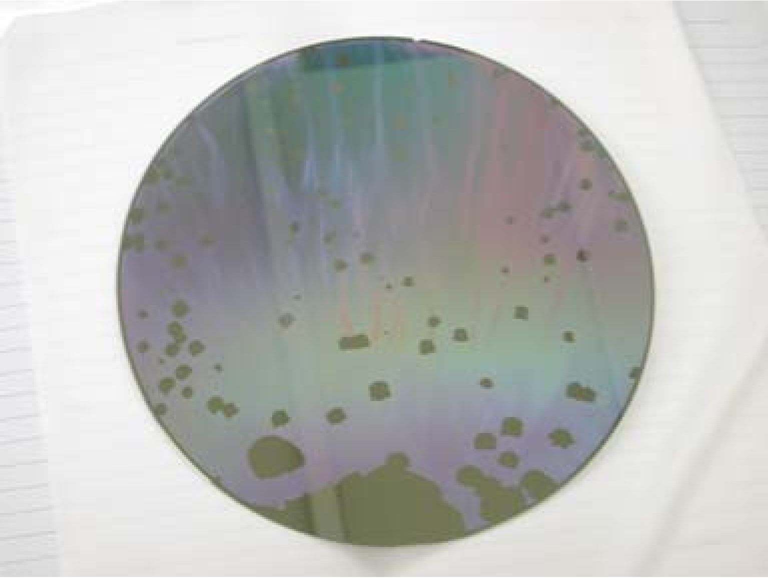


boiling point at about 232°C and an equivalent 5.5:1 mixing ratio (86%H_2SO_4; 3%H_2O_2;11%H_2O)

Results on Implanted Photoresist

2.5×10^{14} ions/cm^2, 40 keV As Implant

batch spray system



⇒

20 min Standard POU SPM
→ Resist Still Present

5.5 min Steam-Injected SPM
→ Resist Stripped

Time to clear blanket 2.5×10^{14} ions/cm^2, 40keV As implanted photoresist dropped from 50 min SPM to 5.5 min SPM

All-Wet PR Strip with Low Material Loss

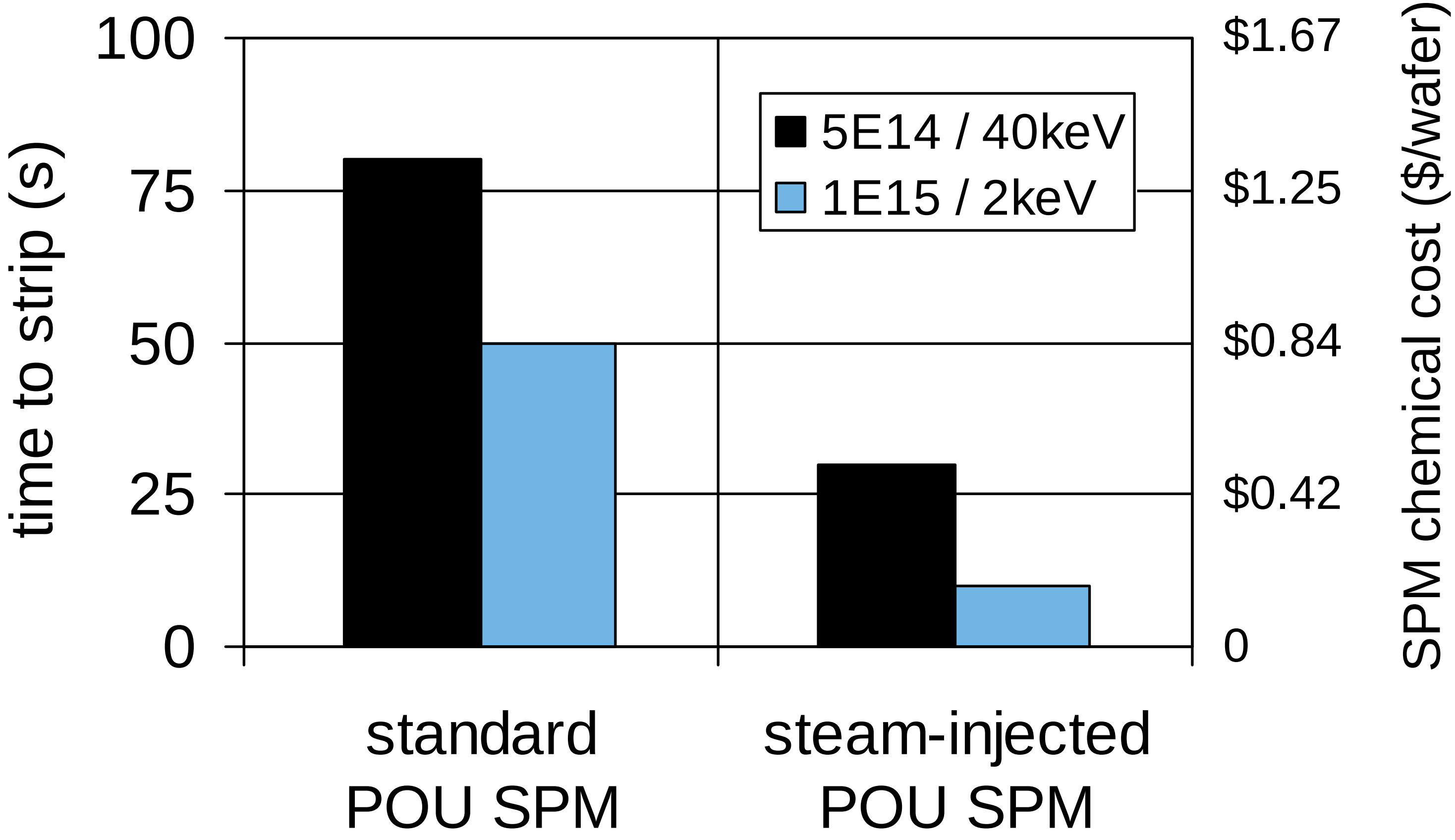
FSI ZETA® System (Batch Spray) with ViPR™ Technology for Steam-Injected SPM Stripping Implanted Photoresist

Dose (ion/cm^2)	Energy & species	SPM time (min)	oxide loss (Å)
5x10^{14}	40keV As	4	<0.2
1x10^{15}	2keV As	4	<0.2
3x10^{16}	7keV BF$_3$ (PLAD)	4	<0.2

LDD implant
ITRS indicates
<0.3 Å

Very Fast Single-Wafer Photoresist Stripping

80% Reduction in Time and Cost for Single Wafer Stripping of Arsenic-implanted Photoresist



[standard SPM = POU mixing with 150°C sulfuric acid]

Summary

- Sulfuric acid – hydrogen peroxide mixture continues to be a common approach to all-wet implanted PR strip
- Trade-off between POU heat of mixing temperature gain and dilution effect
- Patent-pending Steam-Injected SPM process provides increased temperature at the wafer surface with minimal dilution
- Steam-Injected SPM process meets ITRS material loss requirements for LDD implants