Role of Glycine-H_2O_2 in Chemical Mechanical Polishing of Copper

V. R. Gorantla, Z. Lu, S. Hegde, E. Matijević, and S. V. Babu

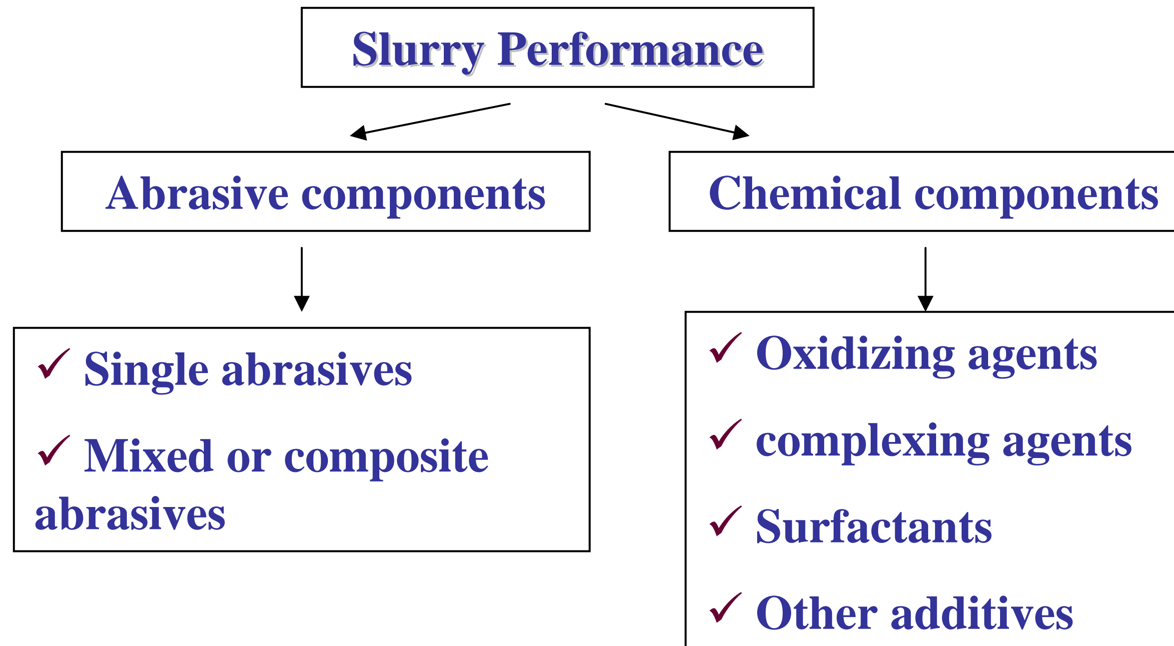
Center for Advanced Material Processing

Clarkson University, NY-13699

Outline

- Introduction
- Cu-H_2O_2-glycine interactions
- Packed bed column technique to study chemical and Cu interactions
- Summary
- Acknowledgments

Introduction



For effective integration of low-k materials with copper interconnects:

Copper CMP has to become a more chemically driven process rather than mechanically driven process

Introduction (contd..)

Fundamental understanding of chemicals and copper film interactions are necessary to develop slurries that provide:

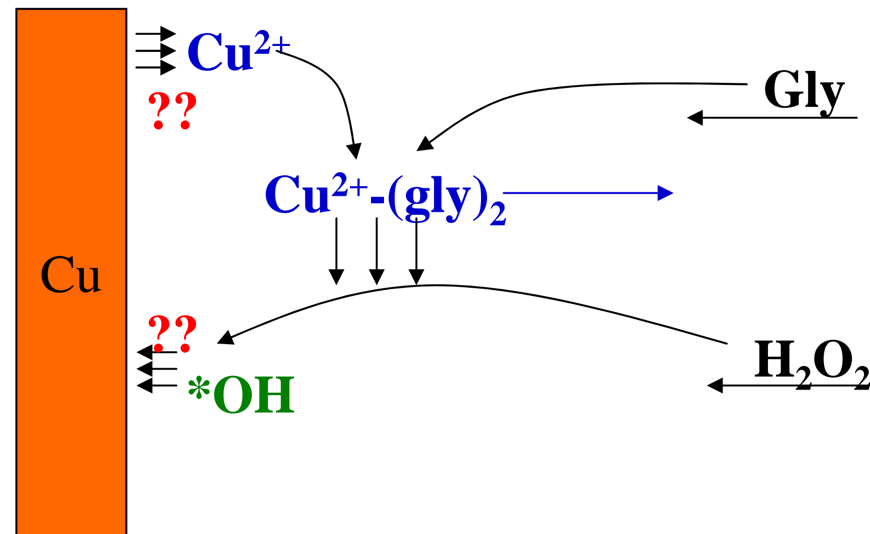
- **High removal rates**
- **Fewer defects – Corrosion pits, Galvanic effects**

Chemical factors that play important role during Cu CMP

- ✓ Chemical interactions between various chemical additives
- ✓ pH of the slurry
- ✓ Nature and properties of the modified surface layer during Cu CMP

Mechanism of Cu removal in glycine-H_2O_2 system

(M.Hariharaputhiran et al; J. of Electrochem. Soc. 147 (10) 3820-3826 (2000))



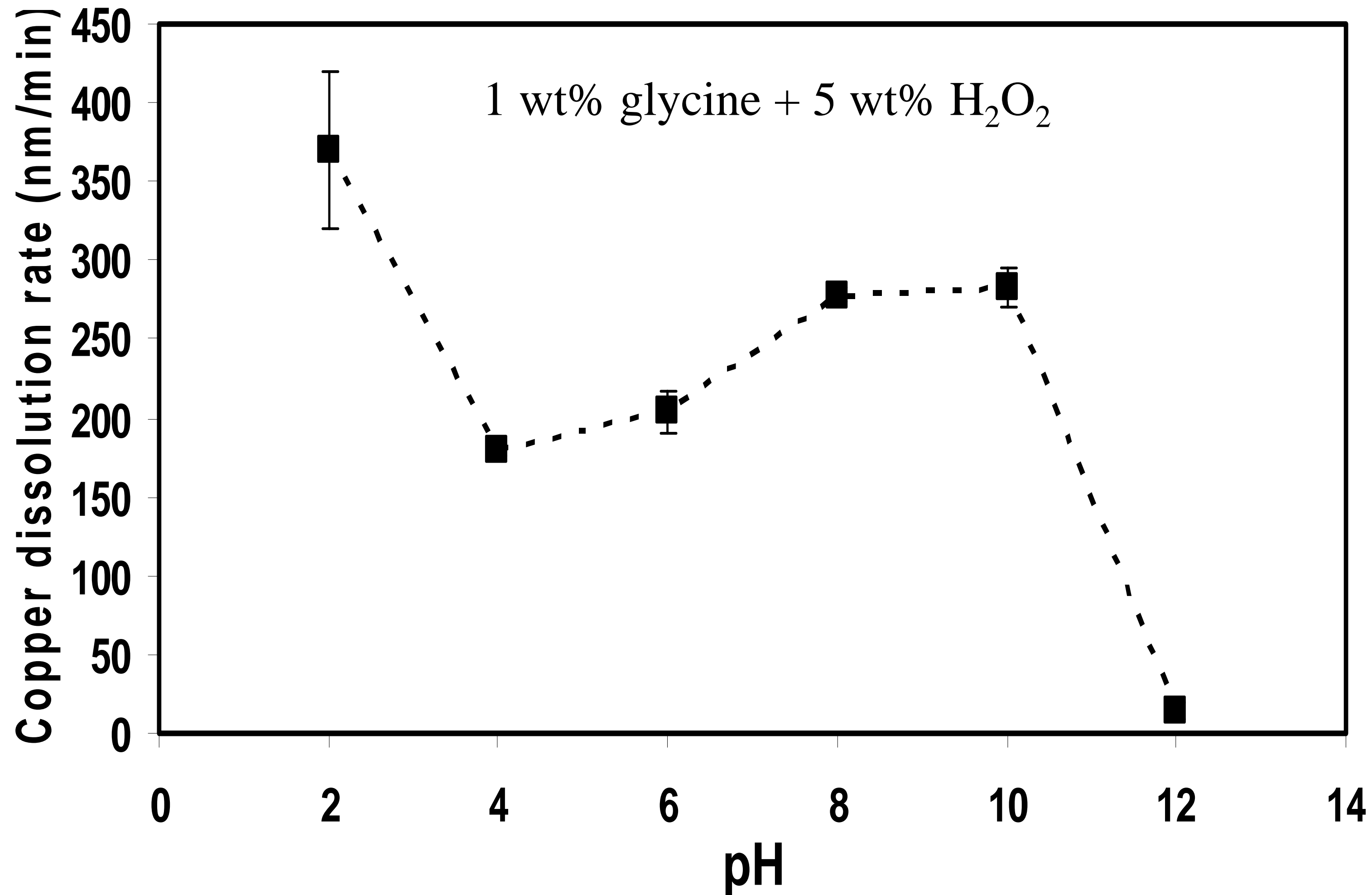
✓ **Cu-$(Gly)_2$ complex catalyzes the decomposition of H_2O_2 to [*OH] radicals.**

✓ **[*OH] radicals are powerful oxidizing agents than H_2O_2.**

✓ **Hydroxyl radicals enhance the removal rates of copper during CMP in glycine-H_2O_2 based slurries**

- *OH trapping experiments were performed at pH ~8.0
- Increase in Cu^{2+} ion concentration in glycine-H_2O_2 system at pH ~ 8 showed an increase in [*OH]
- Cu dissolution rates also increased with increase in Cu^{2+} concentration in glycine-peroxide solution at pH ~8
- However, the mechanism at other pH values was not tested

Effect of pH on Cu dissolution rates



pH has a strong effect on Cu dissolution rates

Effect of Cu^{2+} concentration on Cu dissolution rates

Solution composition	**pH of the solution**	**Cu dissolution rates (nm/min)**
1 wt% glycine + 5 wt% H_2O_2 + 0.06 wt% $Cu(NO_3)_2$	3.7	225 ± 3
1 wt% glycine + 5 wt% H_2O_2 + 0.125 wt% $Cu(NO_3)_2$	3.4	245 ± 7
1 wt% glycine + 5 wt% H_2O_2 + 1.0 wt% $Cu(NO_3)_2$	2.6	365 ± 9

Cu dissolution rates increased with increase in [Cu^{2+}] in glycine-H_2O_2 system

However, there is change in the pH of the solution (decrease in pH with increasing Cu^{2+} concentration)

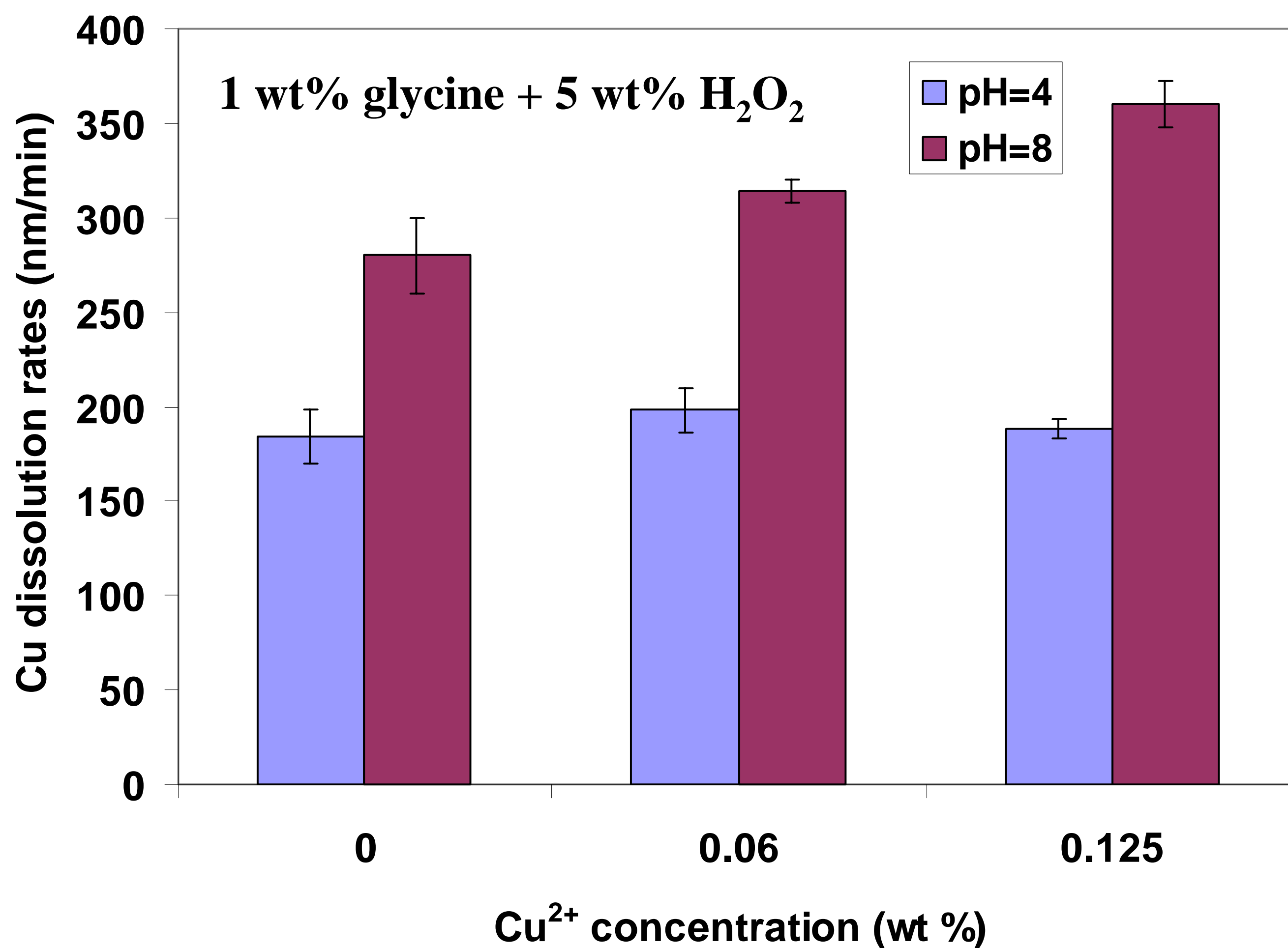
Which factor controls Cu dissolution? pH / *OH radicals

Cu dissolution experiments

Solution composition	**Natural pH of the solution in Column-1**	**Cu dissolution rates in the solutions of Column-1**	**Cu dissolution rates in 1 wt% glycine + 5 wt% H_2O_2 without $Cu(NO_3)_2$**
1 wt% glycine + 5 wt% H_2O_2 + 0.06 wt% $Cu(NO_3)_2$	3.7	225 ± 3	205 ± 3
1 wt% glycine + 5 wt% H_2O_2 + 0.125 wt% $Cu(NO_3)_2$	3.4	245 ± 7	250 ± 3
1 wt% glycine + 5 wt% H_2O_2 + 1.0 wt% $Cu(NO_3)_2$	2.6	365 ± 9	340 ± 42

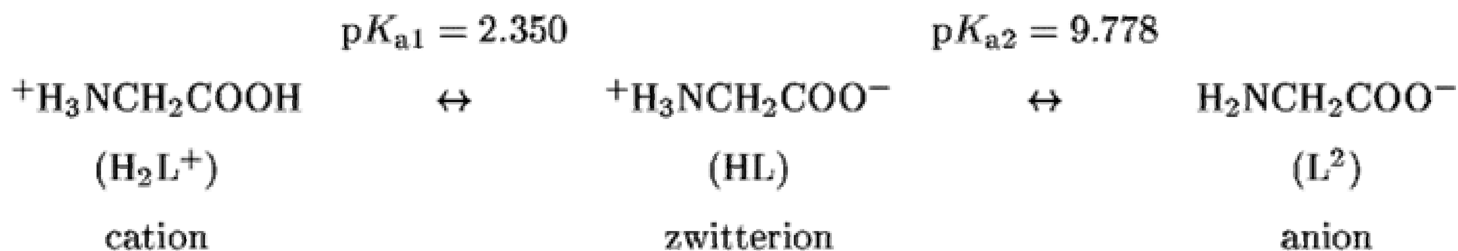
pH of the solution controls Cu dissolution rates in acidic conditions

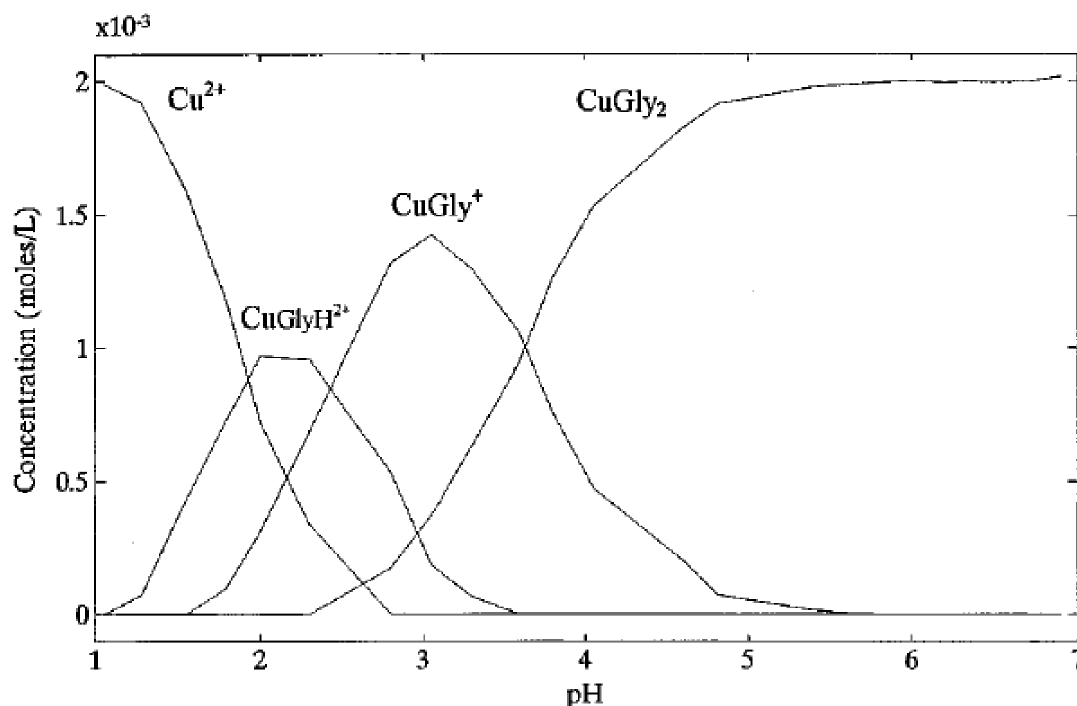
Comparison of copper dissolution rates in glycine-H_2O_2 system containing Cu^{2+} ions at pH 4.0 and pH 8.0



Addition of Cu^{2+} ions has an effect on copper dissolution rates at pH 8, but not at pH 4

Effect of pH on Cu^{2+} and glycine reactivity in aqueous solutions

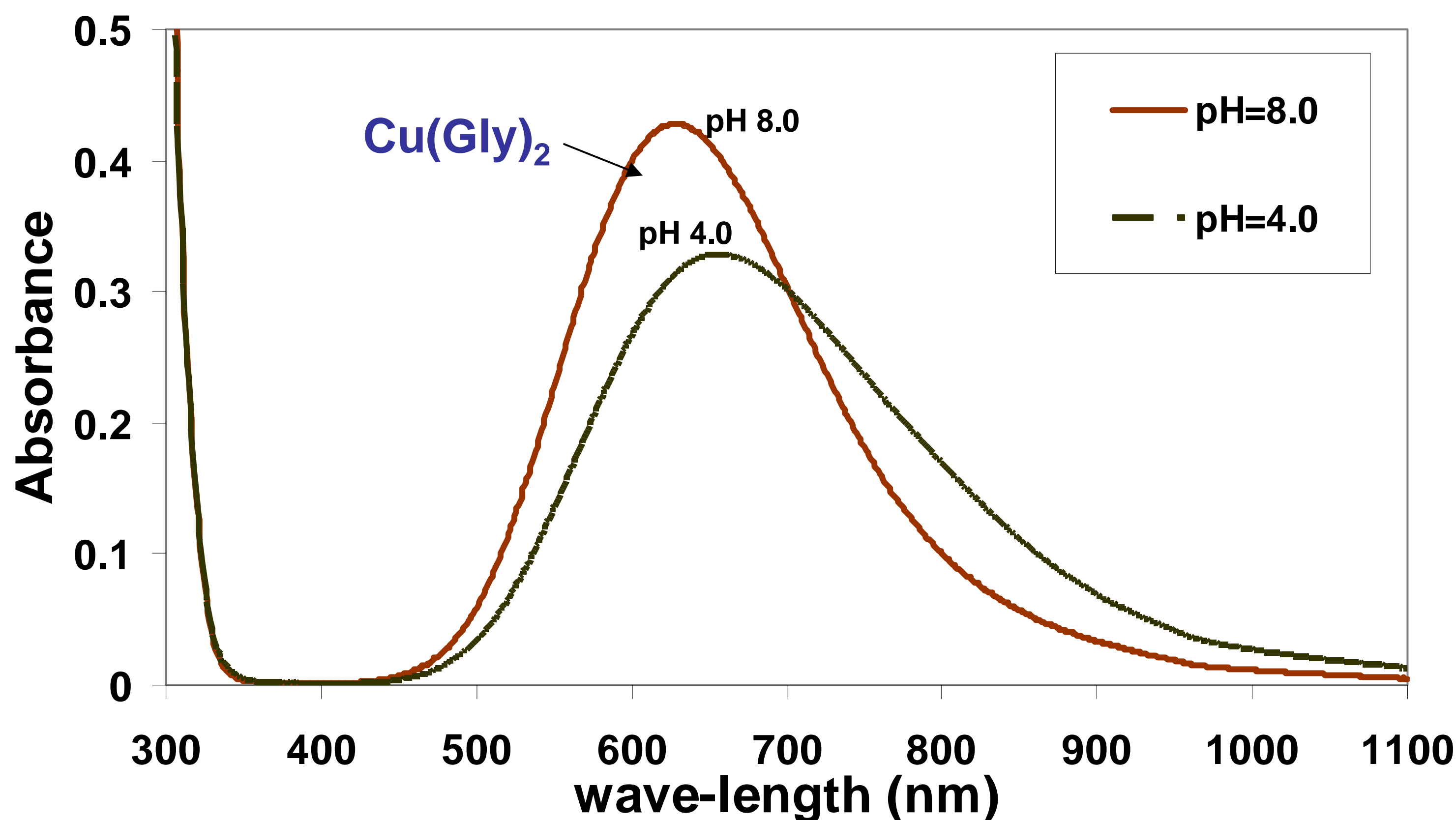




Calibrated concentration profiles of [0.002 M] Cu(II) and 0.5 M Glycine

(M.M.Darj and E.R.Malinowski, Anal. Chem. 1996, 68, pp 1593-1598)

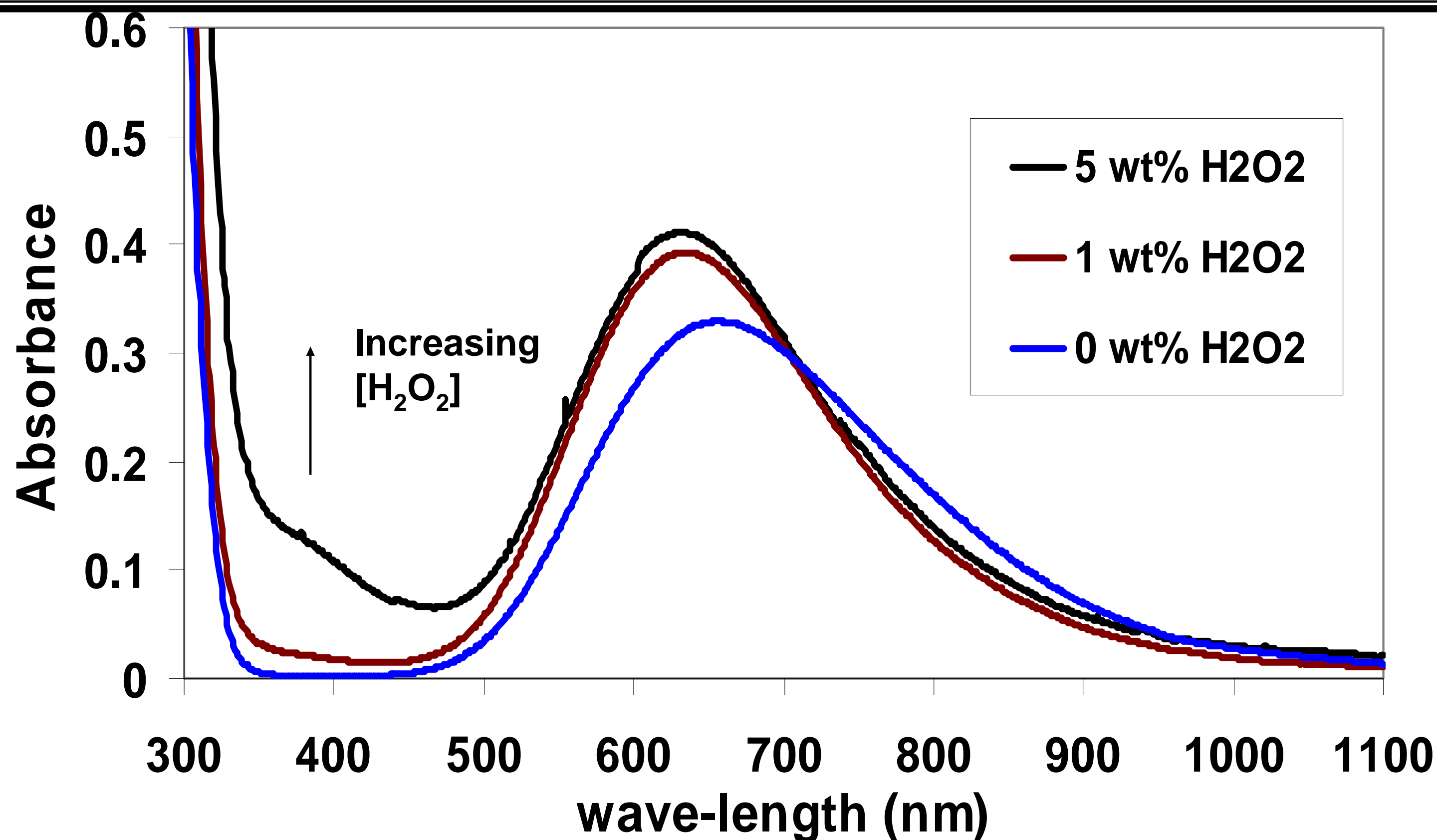
UV/Vis spectroscopy of (Cu^{2+}-glycine) in aqueous solutions in the absence of H_2O_2 as a function of pH



Different Cu^{2+}-glycine species at pH 4 and 8 in the absence of H_2O_2

DI water as reference; Solution composition: [0.01 M Cu^{2+} + 0.1 M Glycine]

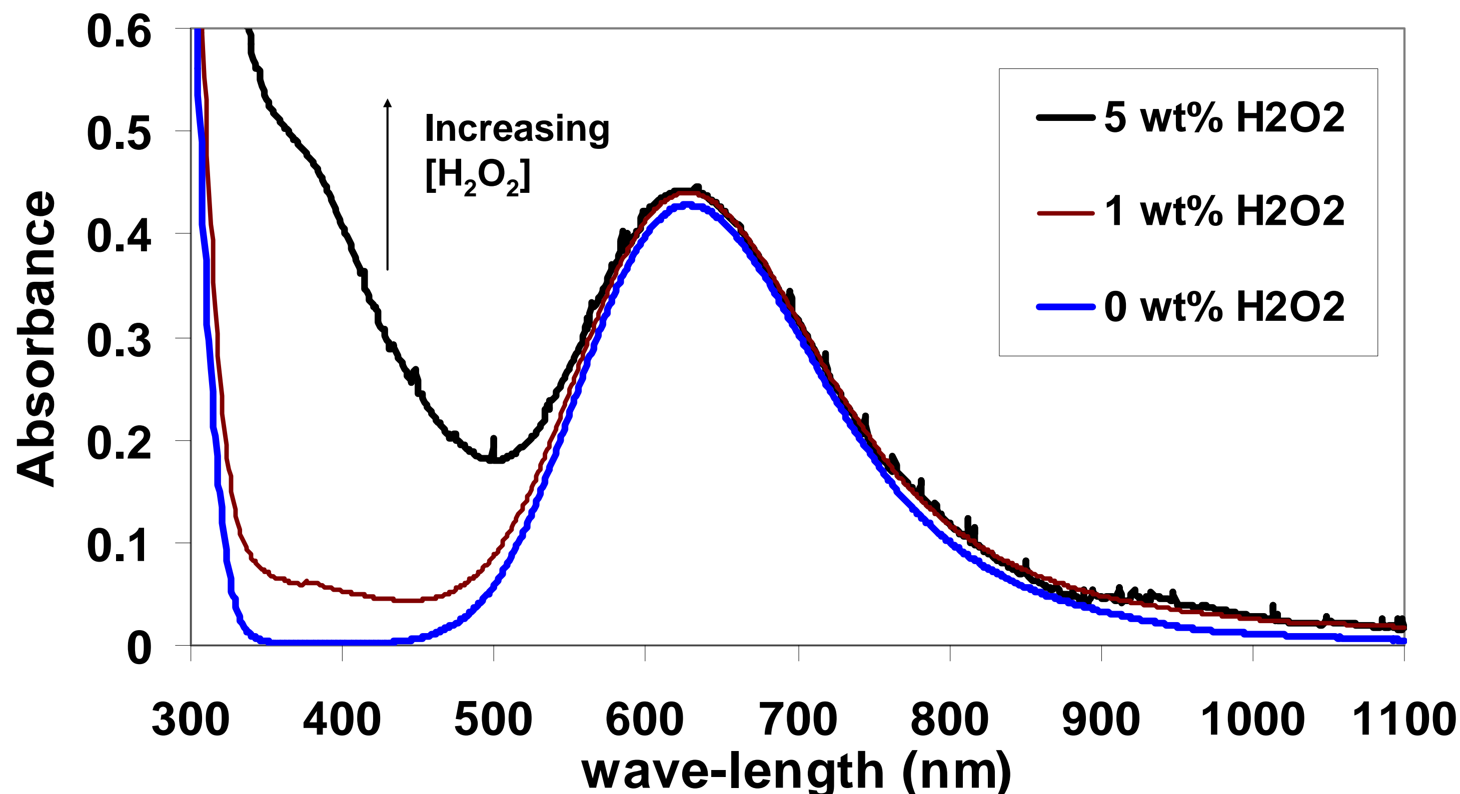
UV/Vis spectroscopy of (Cu^{2+} - Glycine - H_2O_2) in aqueous solution as a function of H_2O_2 concentration at <u>pH = 4</u>



- $Cu(Gly)_2$ complex prevails at pH =4 in the presence of H_2O_2
- Increase in the absorbance at 360 nm with increase in H_2O_2 concentration
- The absorbance at 360 nm represents Cu^{2+}-peroxy-glycine complex

DI water as reference; Solution composition: [0.01 M Cu^{2+} + 0.1 M Glycine + <u>x -wt% H_2O_2</u>]

UV/Vis spectroscopy of (Cu^{2+} - Glycine - H_2O_2) in aqueous solution as a function of H_2O_2 concentration at <u>pH = 8</u>



- Increase in the absorbance at 360 nm with increase in H_2O_2 concentration
- Absorbance intensity at 360 nm, at pH 8 higher than that at pH 4
- No change in the intensity of the peak at 640 nm ($Cu(Gly)_2$)

DI water as reference; Solution composition: [0.01 M Cu^{2+} + 0.1 M Glycine + <u>x -wt% H_2O_2</u>]

Literature on Cu – complexing agent interactions in aqueous solutions containing H_2O_2

T. Kaden, and H. Sigel, *Helvitica Chimica Acta*, 50 (4), p: 947 (1968) **and,**

H. Sigel, C. Flierl, R. Griesser, *J. Am. Chem. Soc*., 91 (5), p: 1061 (1969)

1. Cu^{2+} and complexing agents (CA) like (ethylenediamine /bipyridine) in the presence of H_2O_2 in alkaline solutions form (Cu-peroxy- CA) complex species. Increase in the absorbance intensity at 360 nm indicates the formation of this species.

2. (Cu-peroxy- CA) reacts with H_2O_2 to form O_2 and H_2O and Cu-compounds.

M. H. Robbins and R. S. Drago, *J. Catalysis*, 170, pp 295-303 (1997)

Copper$^{(II)}$-glycine complexes activate H_2O_2 for oxidation of organic substrates through formation of Cu-peroxy complexes.

M. S. Sastry et. al., *J. Inorganic Biochemistry*, 45, pp: 159-167 (1992)

The blue precipitate in the system CuO + Glycine + H_2O_2 was shown by element analysis and ESR to be $[Cu(O_2^{2-})(H_3N^+CH_2COO^-)_2(H_2O)]$

Peroxy group

Experimental techniques ?

Techniques usually used to investigate interactions between chemical and Cu films:

- **Electrochemical experiments (In situ and/or ex situ)**
- **XPS analysis of the films after CMP and dissolution expts**

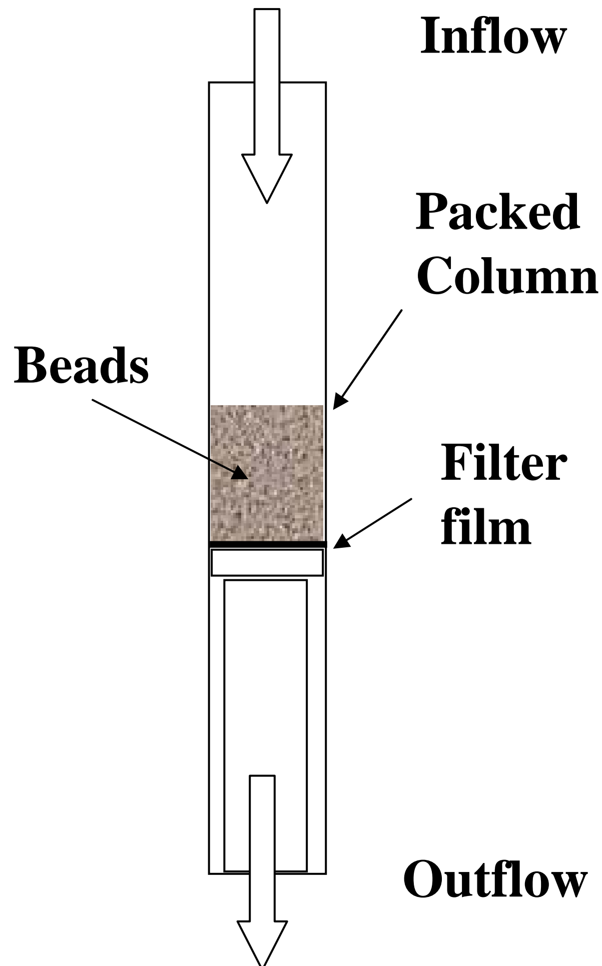
These techniques give us limited information. For example, chemical byproducts formed and their effects on Cu CMP are not observed

In this study we used packed column technique to investigate the interactions between chemicals of the slurry and Cu films.

This packed column technique was used by us to investigate the interactions (adhesion and detachment) between abrasives and metal/dielectric films*.

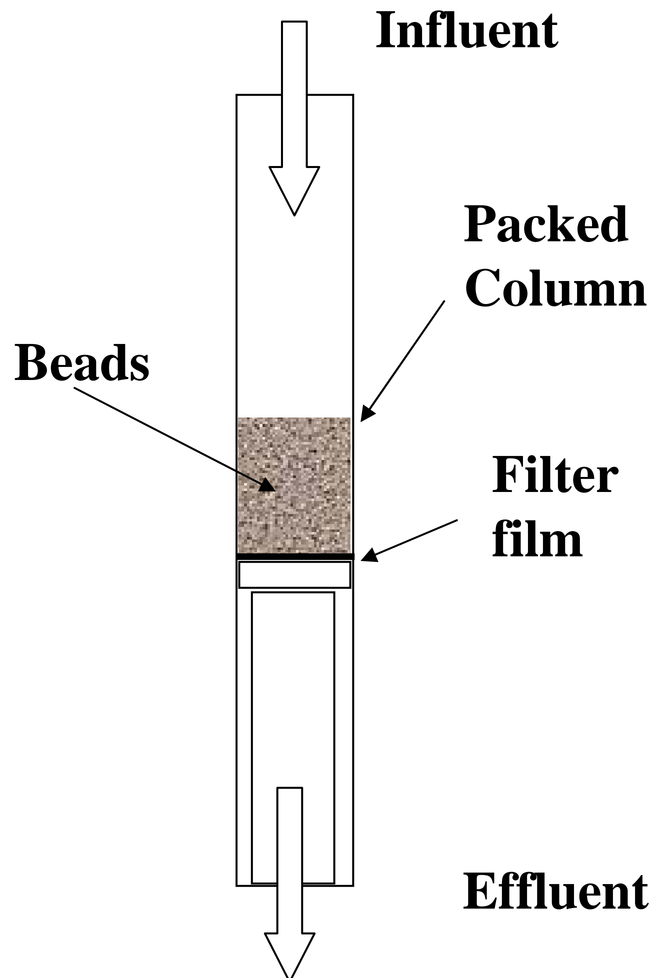
(* Z. Lu, S.V. Babu, and E. Matijević, in MRS spring meeting proceedings, 2003)

Particle deposition and detachment Studies: Packed column technique



- Suspensions: SiO_2, CeO_2, Fe_2O_3, Al_2O_3
- Additives: surfactants, oxidizers, chelating agents, pH regulation agents
- Control temperature and flow rate
- **Beads: Cu, Ta, SiO_2**

Experimental details



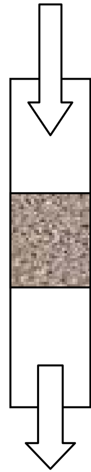
- Height of packed column = ~ 1 cm.
- Avg. Size of copper beads = 80 µm.
- Flow rate = 5 cm^3/min
- Enough void space in the column.

  No filtration effect

- Effluent represents chemical byproducts due to the interactions of chemical additives with Cu film

Experiments with Cu Beads

5 wt% H_2O_2 + 1 wt% glycine, at Natural pH ~5



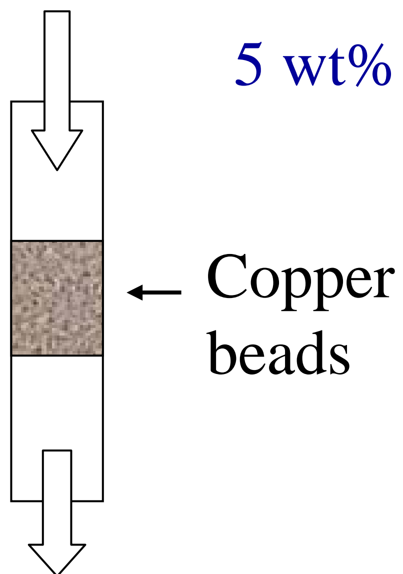
Copper beads

Blue solution

(1) **Dark blue color effluent**
(2) **It turns into green color with aggressive bubbling finally forming a green color precipitate, all within 30 sec**
(3) **pH of the effluent (~7.7) is greater than the influent (~5.0)**
(4) **The effluent is also hot (reactions appear to be exothermic)**

Effluent with green precipitate

Experiments with Cu beads



5 wt% H_2O_2 + 1 wt% glycine, **at pH 8.**

The green precipitate is generated with in 5-10 seconds

Reaction mechanism (Hypothesis)

Cu

Reactions taking place inside the column

Gly

Cu^{2+}

??

Reactions taking place in the bottle

Cu^{2+}-$(gly)_2$

$[Cu^{2+}$-(HO_2^-)-$(gly)_2]$

+ H_2O_2 (Excess)

Green precipitate + O_2

??

*OH

H_2O_2

HO_2^-

More HO_2^- generated with increase in pH

What impact does $\{Cu^{2+}$-(HO_2^-)-$(gly)_2\}$ complex have on CMP of Cu?

CMP experiments on Cu blanket films

Blanket Cu films were polished with 1 wt% glycine + 5 wt% H_2O_2 solutions at pH 5 and 8

Experimental conditions:

Polisher: Westech 372

Wafer size: 6 inch.

Polishing conditions: (Time, Down Pressure (psi), Platen/carrier speed (RPM))

(5 sec, 2 , 40/40) ⟶ (30 sec, 4 , 75/75) ⟶ (5 sec, 2, 40/40)

Ramp up **Polish cycle** **Ramp down**

Case 1: No DI water rinse

Case 2: DI water rinse

CMP of Cu blanket films

Solution composition	Avg. copper polish rate (nm/min)	Avg. surface roughness (nm)	Remarks
1 wt% glycine + 5 wt% H_2O_2 at pH = 5	225	0.9 (few corrosion patches)	No rinse during the polish ramp down step
1 wt% glycine + 5 wt% H_2O_2 at pH = 8	280	2.0 (Reddish brown patches)	
1 wt% glycine + 5 wt% H_2O_2 at pH = 5	180	0.9 (No patches)	5 sec DI water rinse during the polish ramp down step
1 wt% glycine + 5 wt% H_2O_2 at pH = 8	245	1.0 (No patches)	

Corrosion patches on the wafer polished at pH 8. These patches not observed when rinsed with DI water (instead of polish solution) during ramp down step.

Chemical byproducts (Cu-peroxy-glycine complex) generated are corrosive !

Summary

❖ **pH of the solution controls Cu dissolution rates in acidic conditions and strongly alkaline conditions**

❖ **Hydroxyl radicals are important at intermediate pH values**

❖ **Cu-peroxy-glycine complex concentration increases with increase in pH and H_2O_2 concentration**

❖ **The chemical byproducts (Cu-peroxy-glycine complex) may be responsible for corrosion defects during CMP**

- **Effective transportation of these chemical byproducts away from the wafer could reduce defects**

Acknowledgment

This work is supported by
INTEL Corporation and SRC.