Removal Rate Enhancers For Silica-based Ru Barrier Slurry

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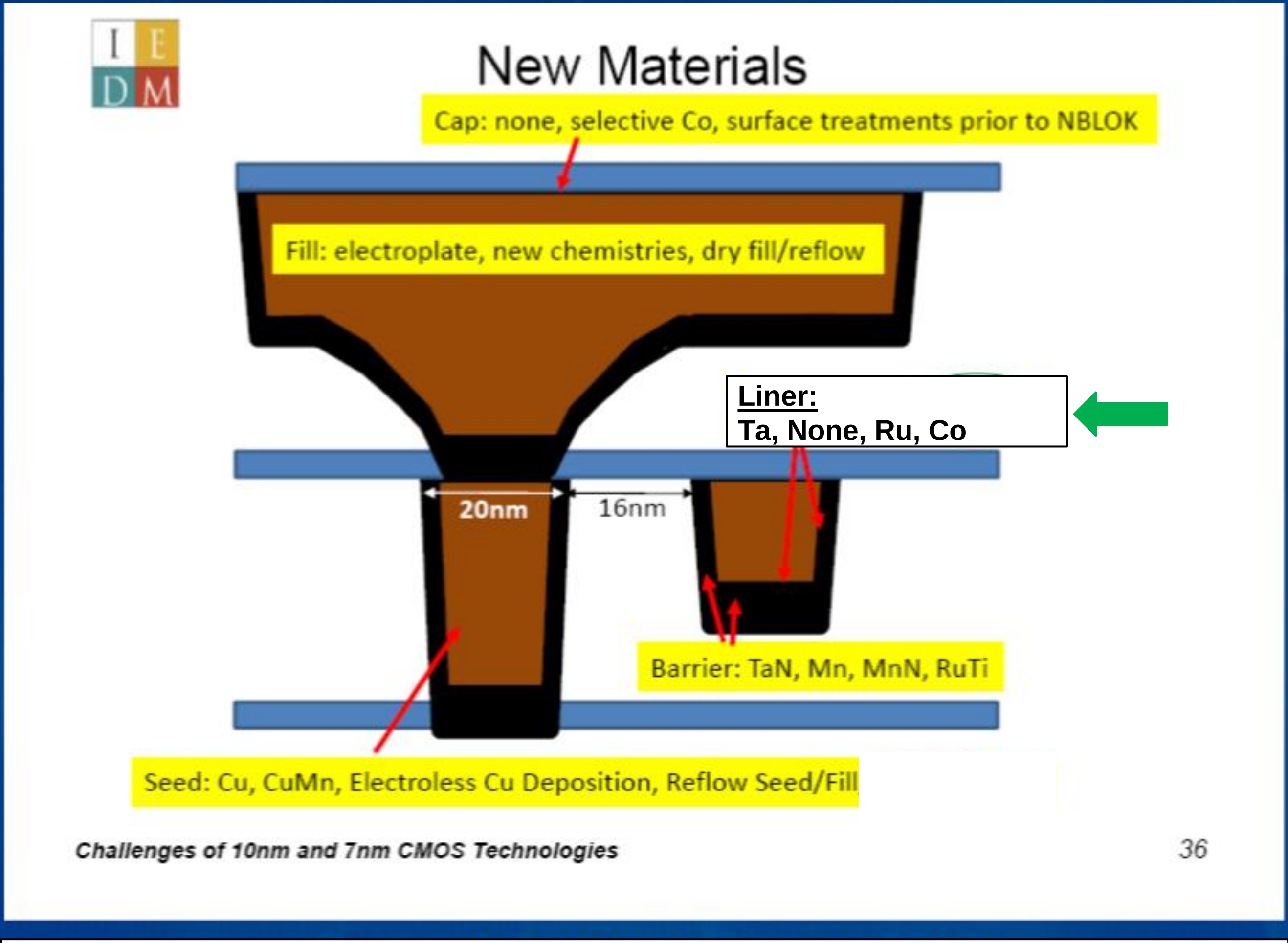
Outline

- **Introduction**
  - Motivation for Ru integration.
  - Targets: > 150 A/min for ≤ 2 psi downforce.
Minimum dielectric loss, lower topo and defects.
  - Slurry design: Identify a complexor enabling higher Ru RR at a lower TEOS:Ru selectivity.
- **Results**
  - Increasing Ru removal rate – colloidal silica + chemistry.
  - TEOS:Ru selectivity improvement by the slurry with complexor B.
  - Lower corrosion current and a higher Ru RR by the slurry with complexor B.
- **Summary**
- **Acknowledgements**

Ru for interconnects



New Materials

Cap: none, selective Co, surface treatments prior to NBLOK

Fill: electroplate, new chemistries, dry fill/reflow

Liner:
Ta, None, Ru, Co

Barrier: TaN, Mn, MnN, RuTi

Seed: Cu, CuMn, Electroless Cu Deposition, Reflow Seed/Fill

Challenges of 10nm and 7nm CMOS Technologies 36

- Ru has lower resistivity than Ta and is less prone to corrosion than Co.
- Ru liner is expected to meet dimensional needs at 7nm.

- Ru or a Ru-based material may be used as a barrier- or liner.

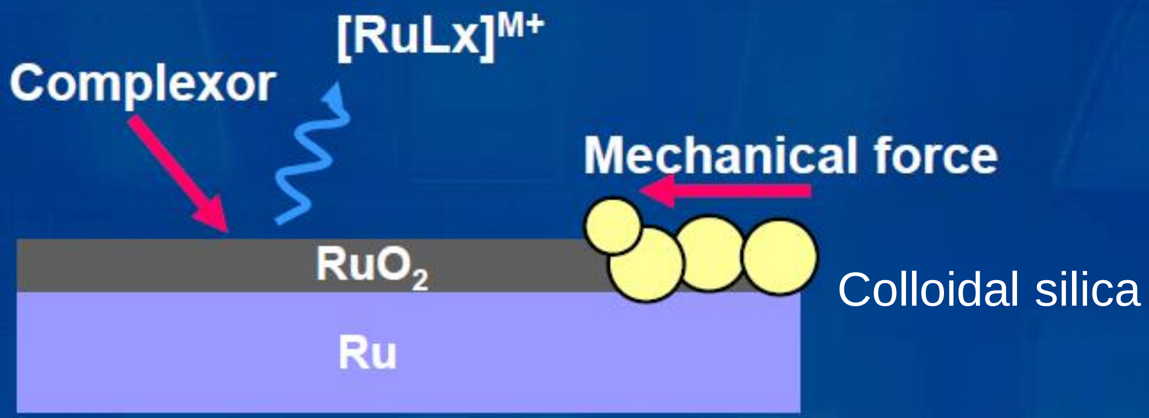
Adapted from “Tokei, IEDM Short Course, 2013”

Targets for Ru barrier slurry

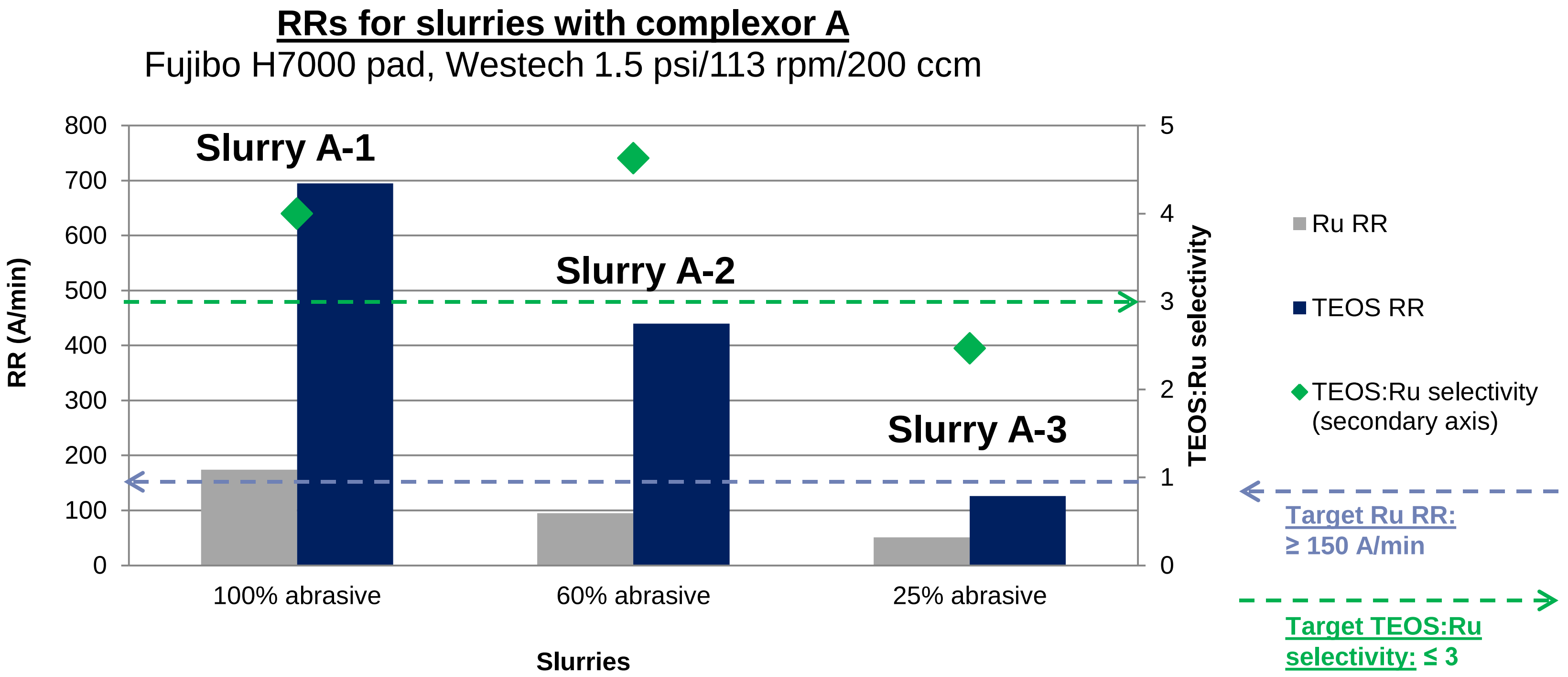
1) Ru removal rate > 150 A/min for ≤ 2 psi downforce.
2) Minimum dielectric film loss
3) Lower topography
4) Lower defects

Ru Slurry Design

- Identify a complexor, Lx, which enhances $[RuLx]^{M+}$ complex formation. These complexes should ideally be fragile surface complex films.

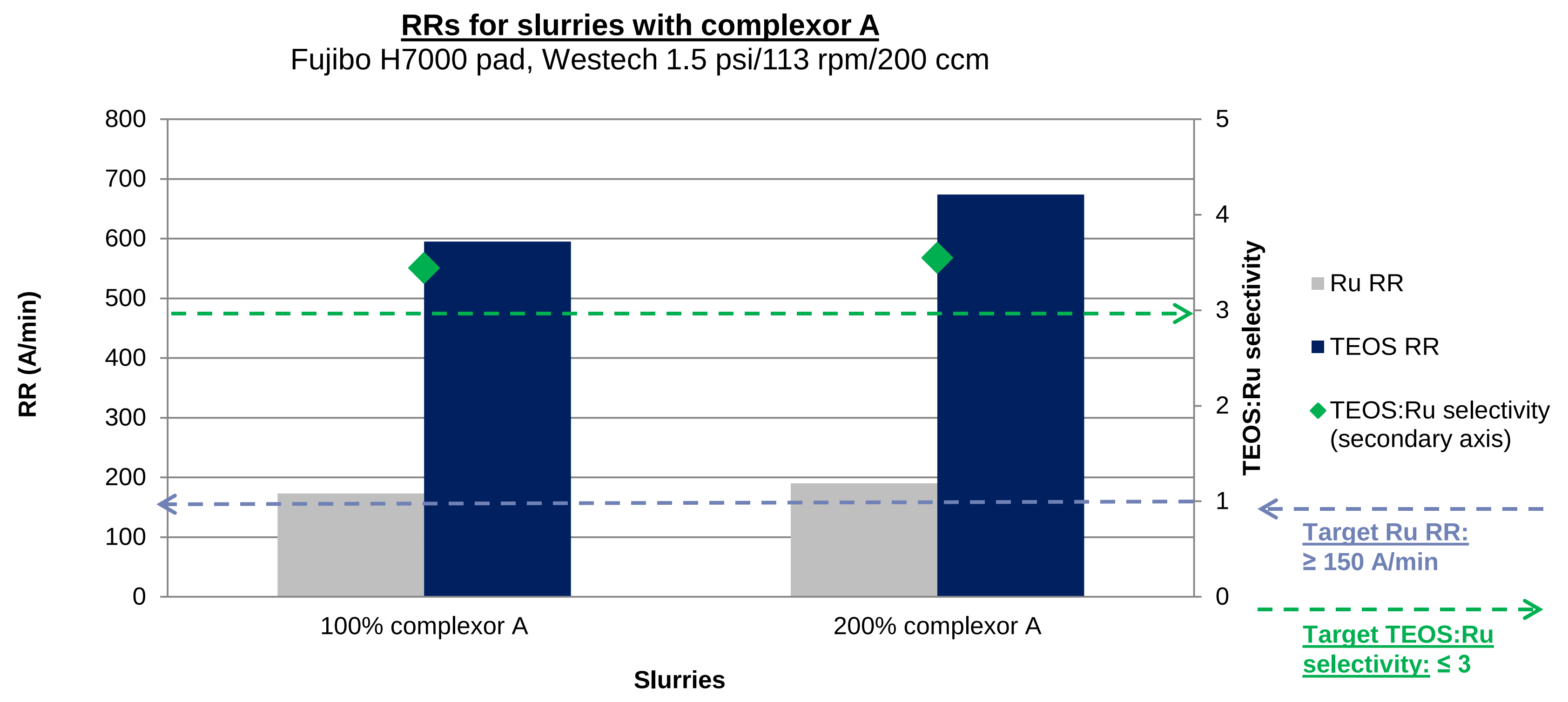


Technical gap 1



- The high TEOS RR of slurry A-1 may result in increased oxide erosion, potentially driving metal loss during overpolish.
- Ru RR should ideally be ≥ 150 A/min, with TEOS:Ru selectivity ≤ 3.
- Slurries A-2 and A-3 do not meet the targets.

Technical gap 2



RRs for slurries with complexor A

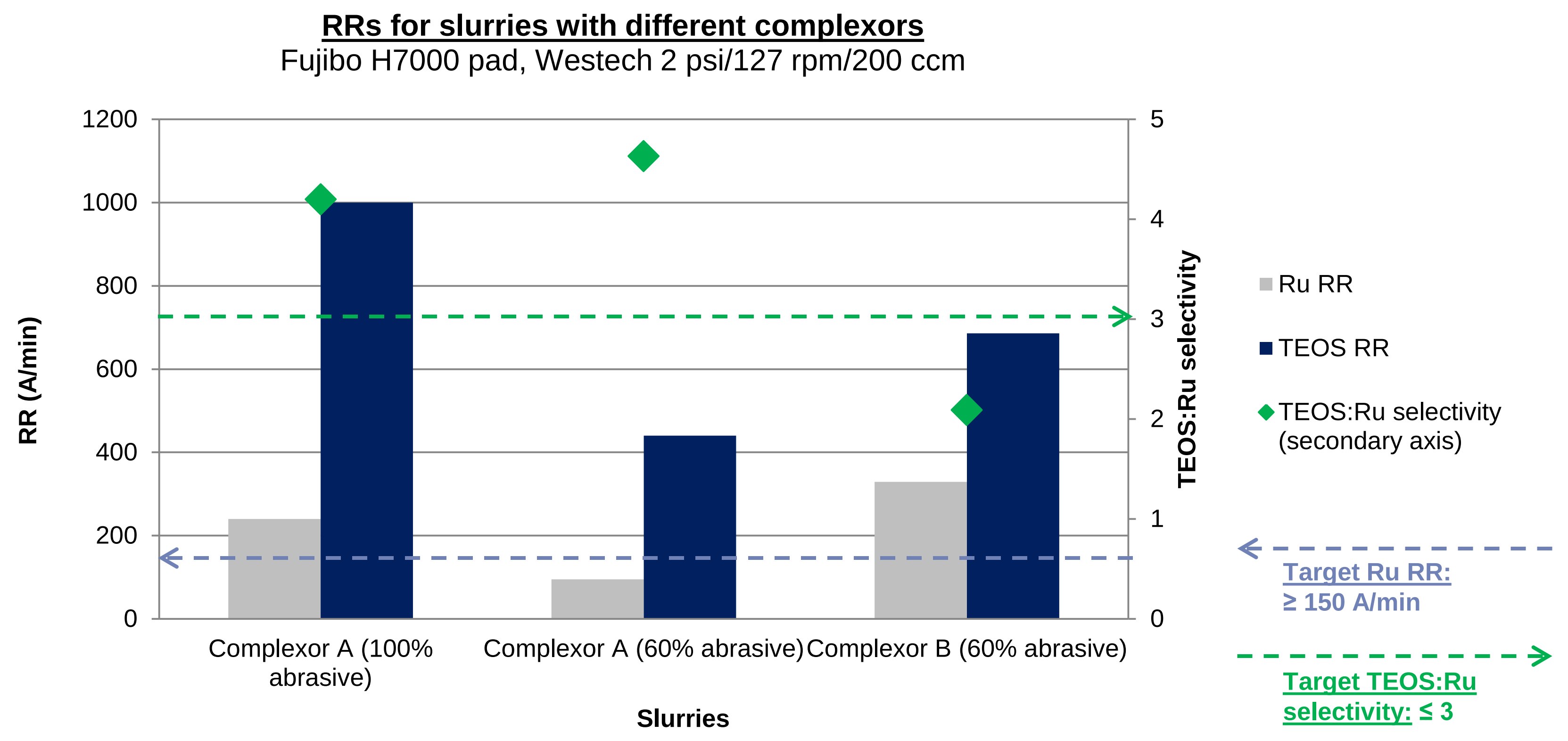
Fujibo H7000 pad, Westech 1.5 psi/113 rpm/200 ccm

Target Ru RR: ≥ 150 A/min

Target TEOS:Ru selectivity: ≤ 3

- **2x higher complexor A concentration does not result in a significant change in Ru RR and TEOS:Ru selectivity.**

Improved Ru RR with complexor B



RRs for slurries with different complexors

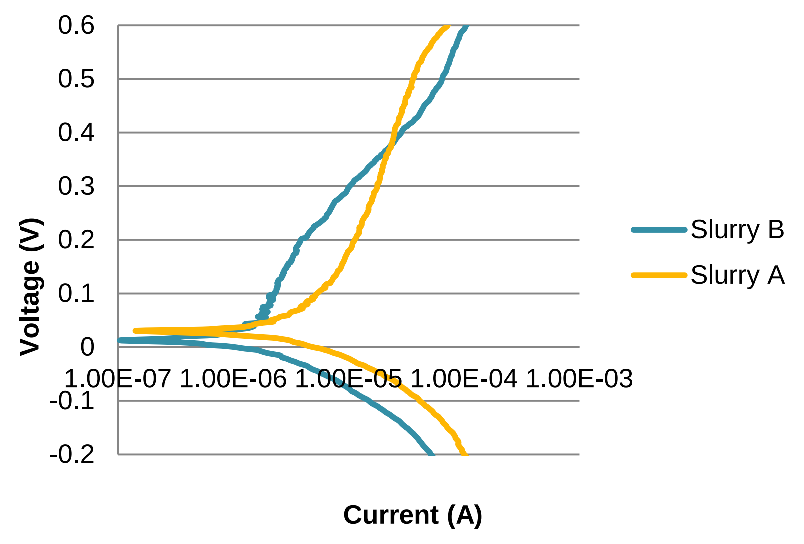
Fujibo H7000 pad, Westech 2 psi/127 rpm/200 ccm

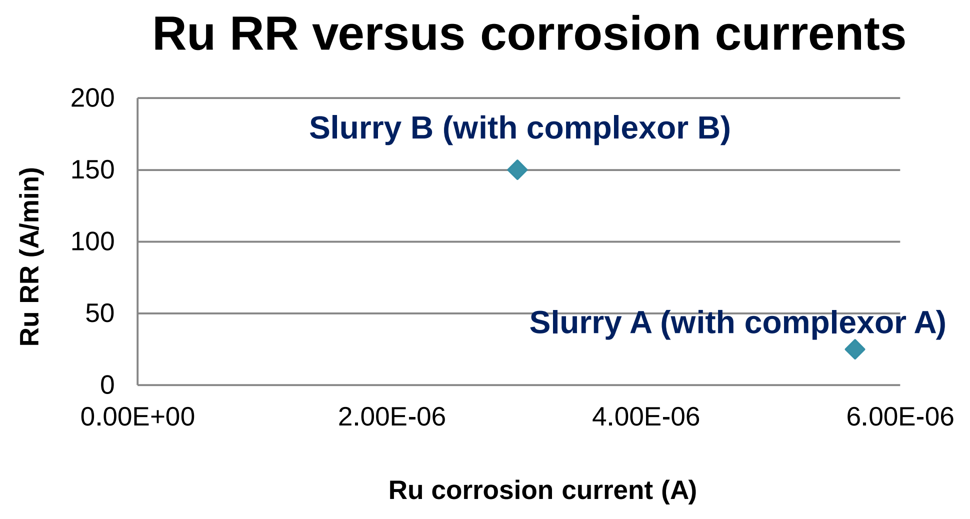
Target Ru RR: ≥ 150 A/min

Target TEOS:Ru selectivity: ≤ 3

- **Complexor B enables a high Ru RR with reduced TEOS:Ru selectivity.**

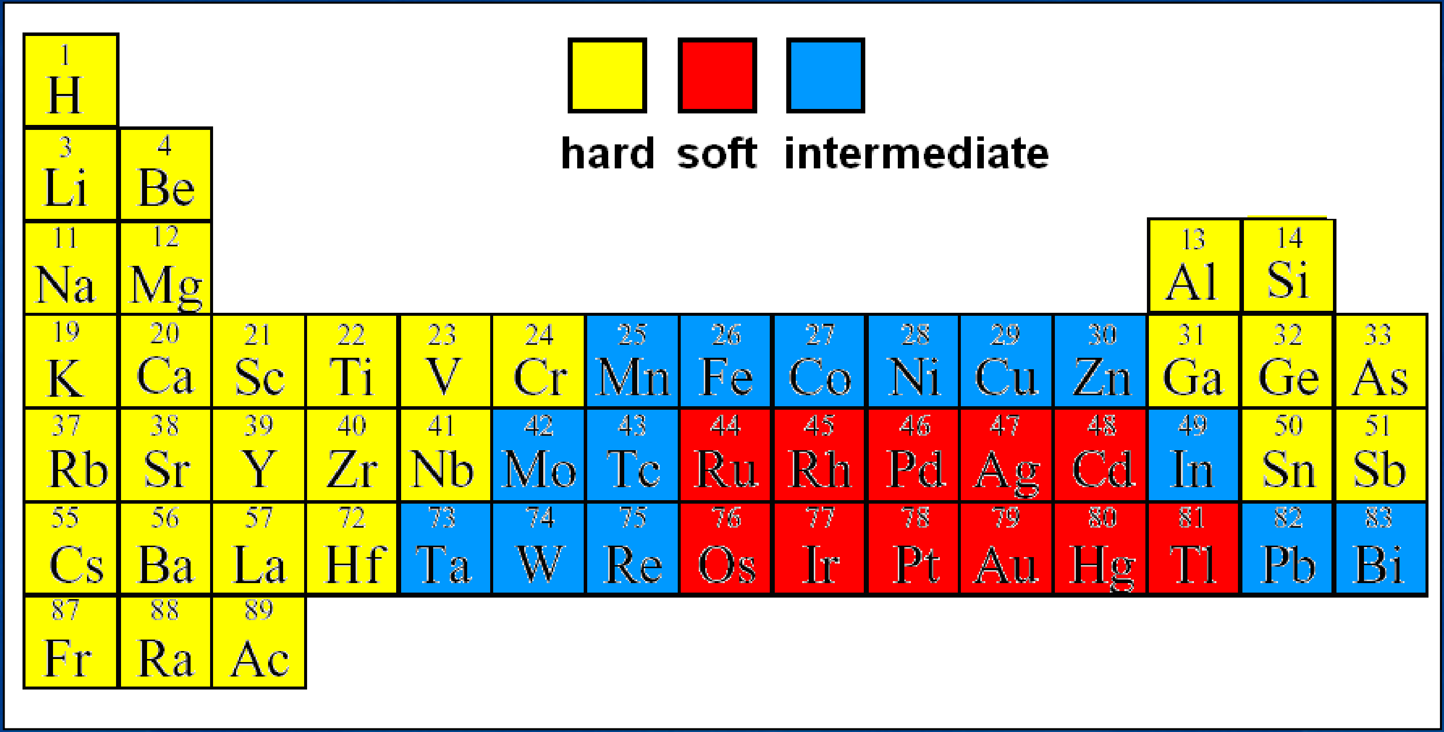
Tafel plot and corrosion currents for Ru





- Slurry A and slurry B are similar w.r.t ΔE (difference in open circuit potential).
- Slurry B (with complexor B) exhibits a higher Ru RR with a lower corrosion current.
- Oxidation of Ru is not driving RR.

HSAB Working model for selectivity improvement



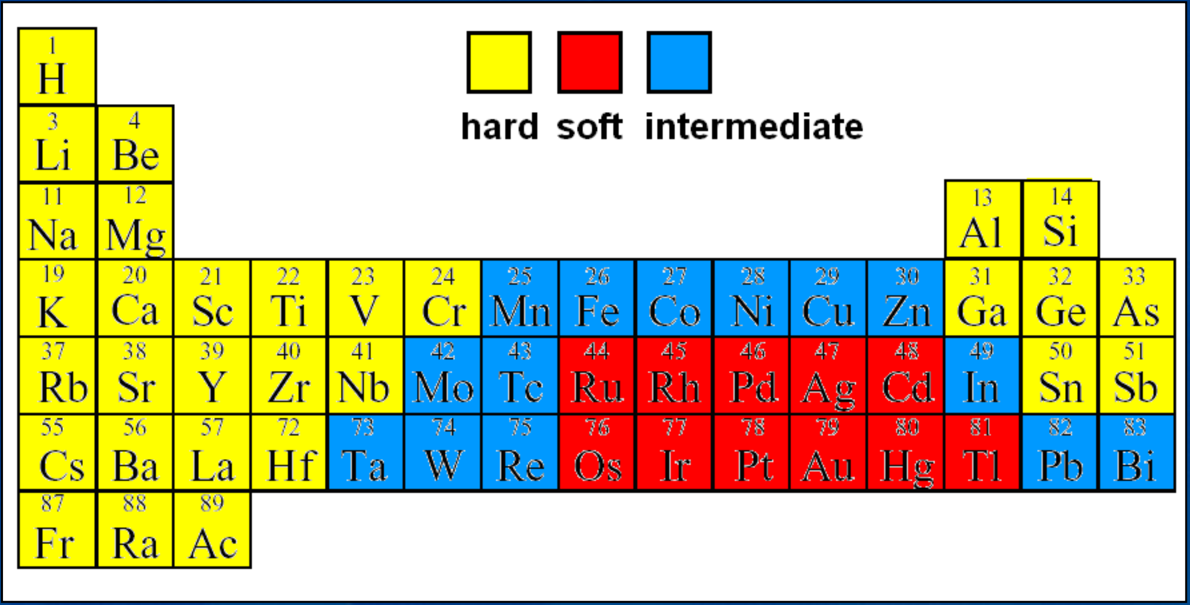
🟨 hard 🟥 soft 🟦 intermediate

1 H														
3 Li	4 Be													
11 Na	12 Mg											13 Al	14 Si	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi
87 Fr	88 Ra	89 Ac												

- HSAB (Hard soft acids and bases) theory.

- “Hard” species, e.g. Al, are weakly polarizable.
- “Soft” species, e.g. Ru, are strongly polarizable.

HSAB theory applied to Ru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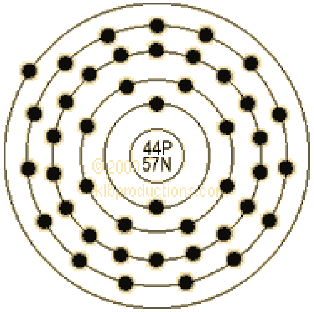
37 Rb 🟨	38 Sr 🟨	39 Y 🟨	40 Zr 🟨	41 Nb 🟨	42 Mo 🟦	43 Tc 🟦	44 Ru 🟥	45 Rh 🟥	46 Pd 🟥	47 Ag 🟥	48 Cd 🟥	49 In 🟦	50 Sn 🟨	51 Sb 🟨
55 Cs 🟨	56 Ba 🟨	57 La 🟨	72 Hf 🟨	73 Ta 🟦	74 W 🟦	75 Re 🟦	76 Os 🟥	77 Ir 🟥	78 Pt 🟥	79 Au 🟥	80 Hg 🟥	81 Tl 🟥	82 Pb 🟦	83 Bi 🟦
87 Fr 🟨	88 Ra 🟨	89 Ac 🟨												



Soft Ru atom (acceptor)

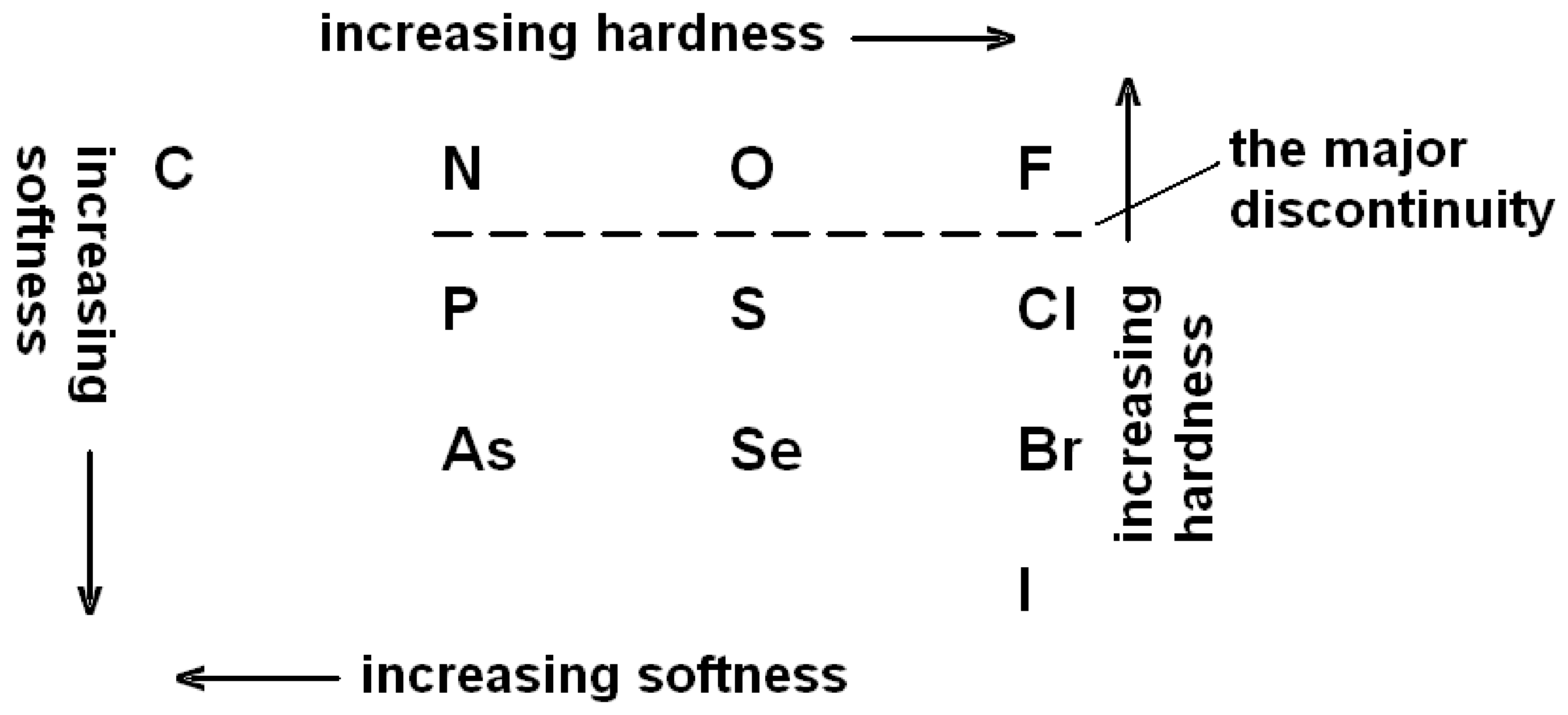
\+

Soft donor (base)

- **In general, *soft* acids react faster and form stronger bonds with *soft* bases, whereas *hard* acids react faster and form stronger bonds with *hard* bases.**

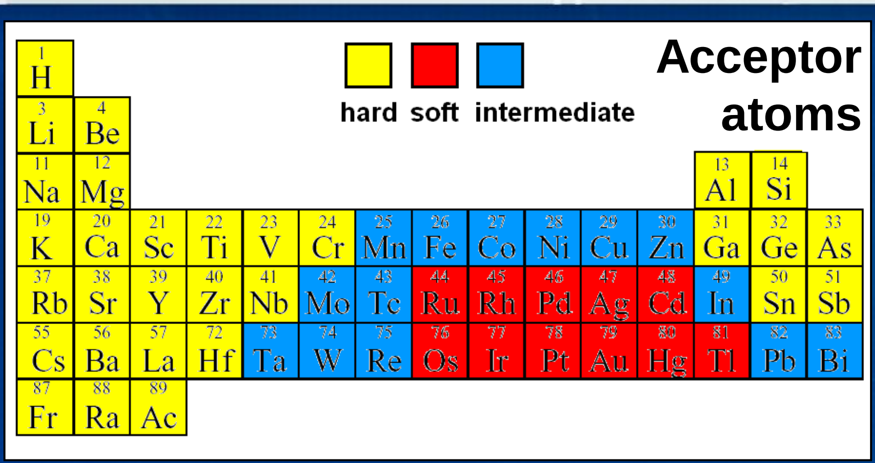
- **A complexor with a soft donor must be identified to enable a complex to be formed with metallic Ru.**

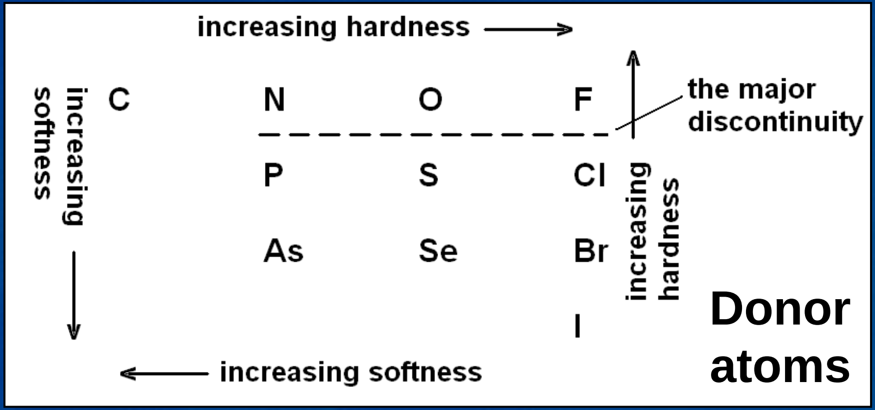
Donor atom(s) for Ru and Ru_xO_y



- Softer donor atoms, e.g. S and P, may work better in complexing metallic Ru.
- The hardness of Ru_xO_y is dependent on the oxidation number of Ru. Donor atom(s) must be chosen to accommodate type of Ru and/or Ru_xO_y to be polished.

Soft donor atom in salt B





Complexor A:

X-R

Complexor B:

Y-R

R = Backbone

X = Hard donor atom

Y = Soft donor atom

- Complexor A does not have a soft donor atom
- A soft donor atom in complexor B may be one commonality which enables an increased Ru RR.

Model for complexor B

R = **Backbone**

X = **Hard donor atom**

Y = **Soft donor atom**

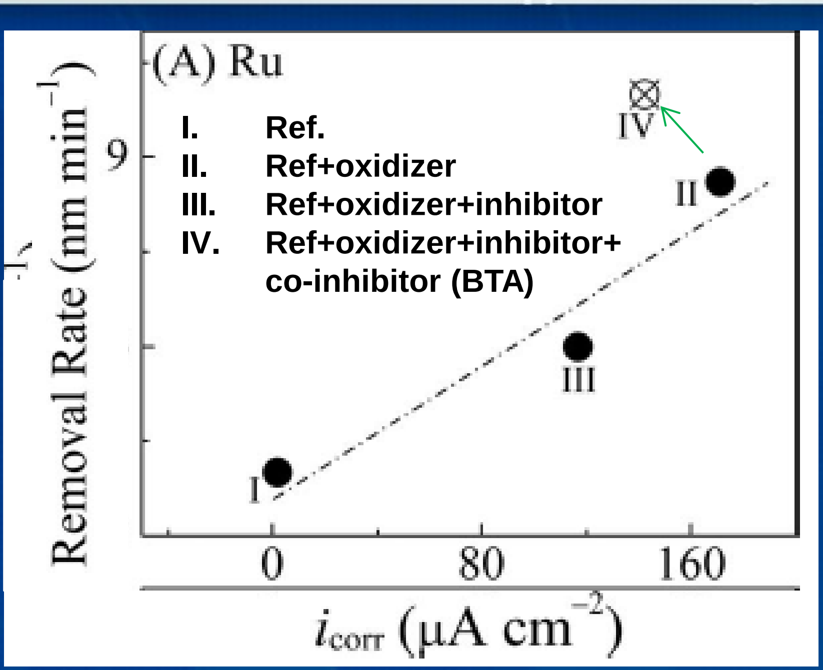
Complexor A:

R-X

Complexor B:

Y-R

Proposed model for Ru removal with Complexor B



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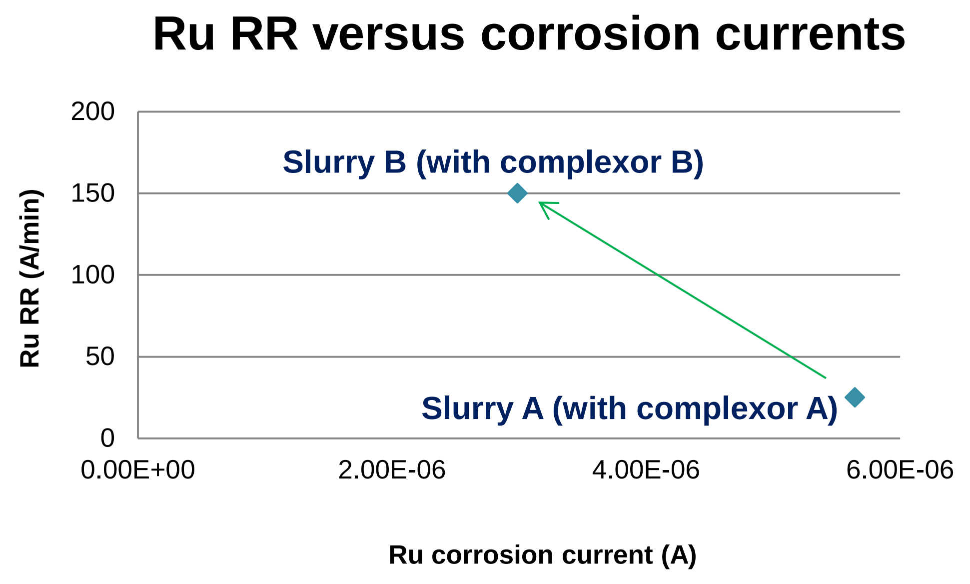

- **In the left plot (a study by Prof. Babu), it is proposed that Ru-BTA complexes are formed through chemical routes without interfacial charge transfer.**
- **There is no BTA in the slurries on the right plot, but it is possible that complexor B (ComB) enables enables formation of [Ru-comB] complexes that form fragile surface complex films in a similar way as Ru-BTA in Prof. Babu's study.**
- **Future work:** **XPS study under consideration.**

Summary

- Colloidal silica based Ru slurry was developed using a Ru complexor approach to enable polish rate and defectivity.
- Complexor B, enabling a higher Ru RR at a lower TEOS:Ru selectivity compared with complexor A, was identified.
- HSAB (hard-soft acids and bases) theory was proposed as a working model to help explain the improved RRs for slurries with complexor B.
- Slurries with complexor B exhibit a higher Ru RR at a lower corrosion current compared with slurries with complexor A, proposing complexor B (comB) enables formation of [Ru-comB] complexes that form fragile surface complex films without interfacial charge transfer.

Acknowledgements

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