Improvement of ESH Impact of Back End of Line (BEOL) Cleaning Formulations Using Ionic Liquids to Replace Traditional Solvents *(Task Number: 425.034)*

PI:

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Cost Share (other than core ERC funding):

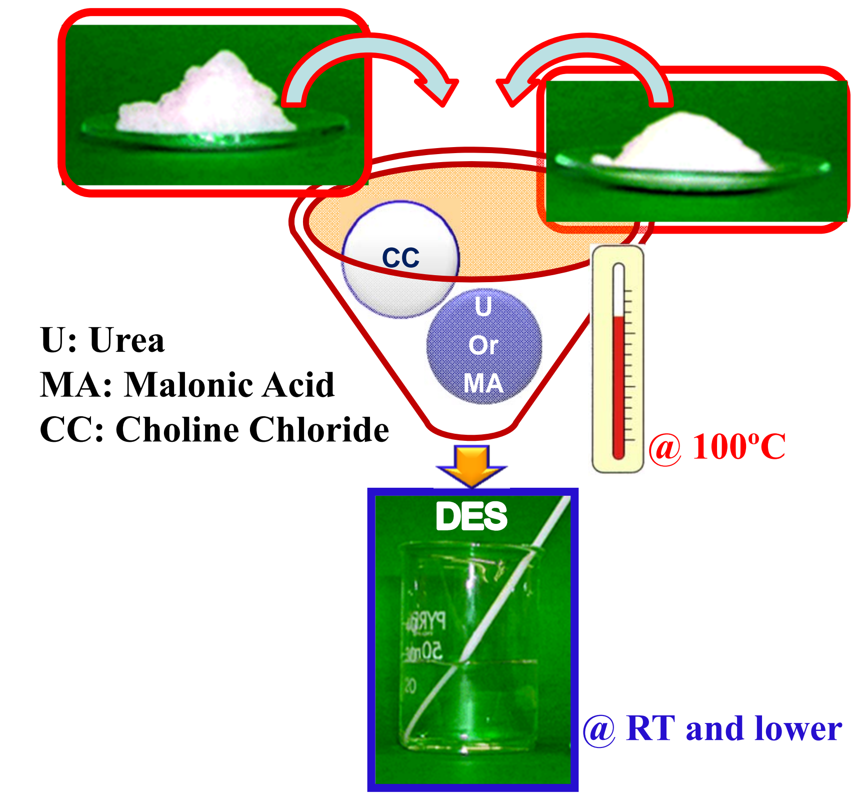
In kind donation of Copper and patterned wafers from Intel and IMEC ($5,000)

Deep Eutectic Solvents (DES)

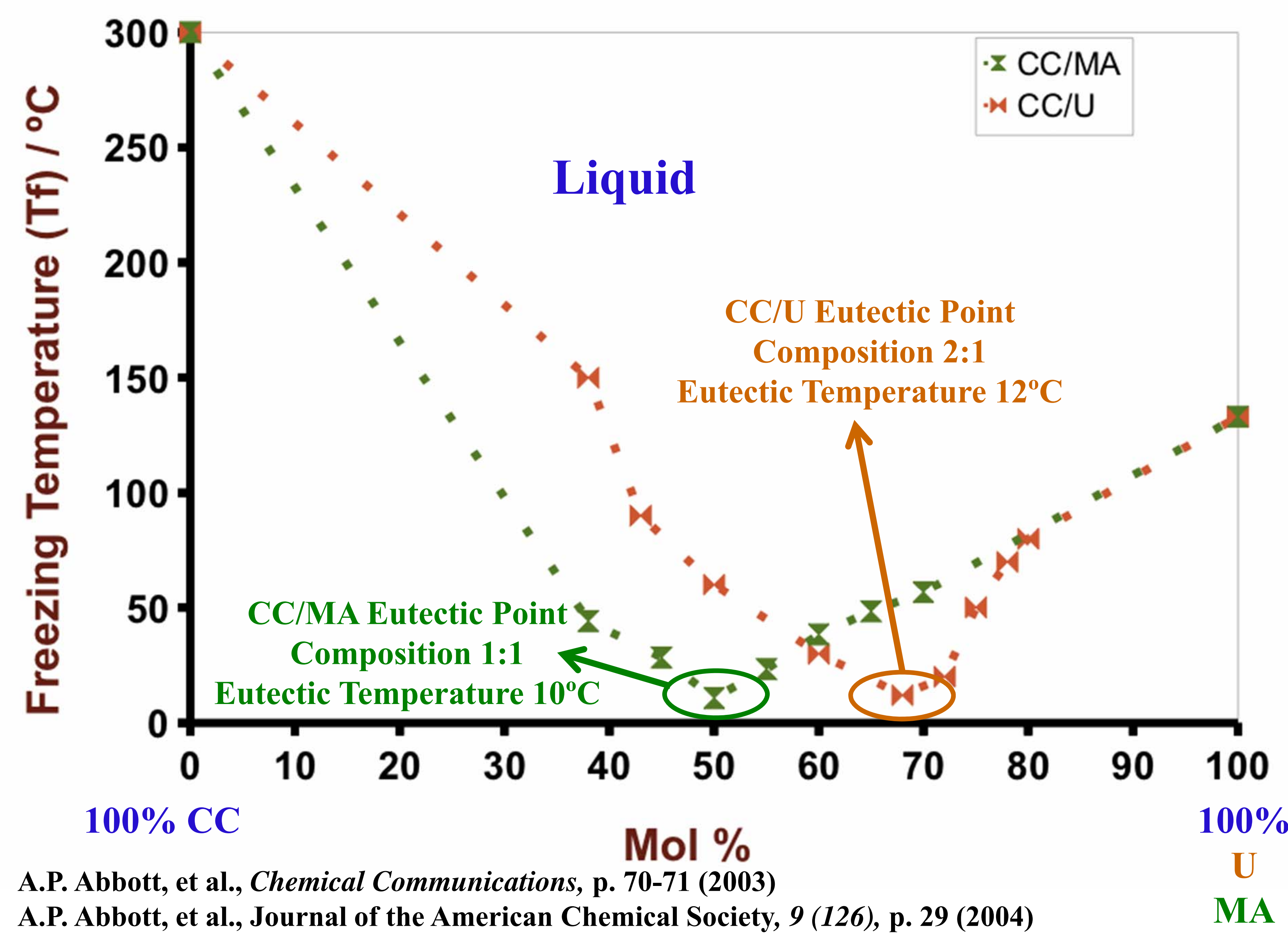
- Ionic mixture which forms an eutectic with a freezing temperature much lower than either of the individual components (quaternary ammonium salts and hydrogen donors)

Properties

- Low vapor pressure
- Low toxicity
- Water soluble
- Dissolve metal oxides
- Low cost



Deep Eutectic Solvents: Binary Phase Diagrams



A.P. Abbott, et al., *Chemical Communications*, p. 70-71 (2003)

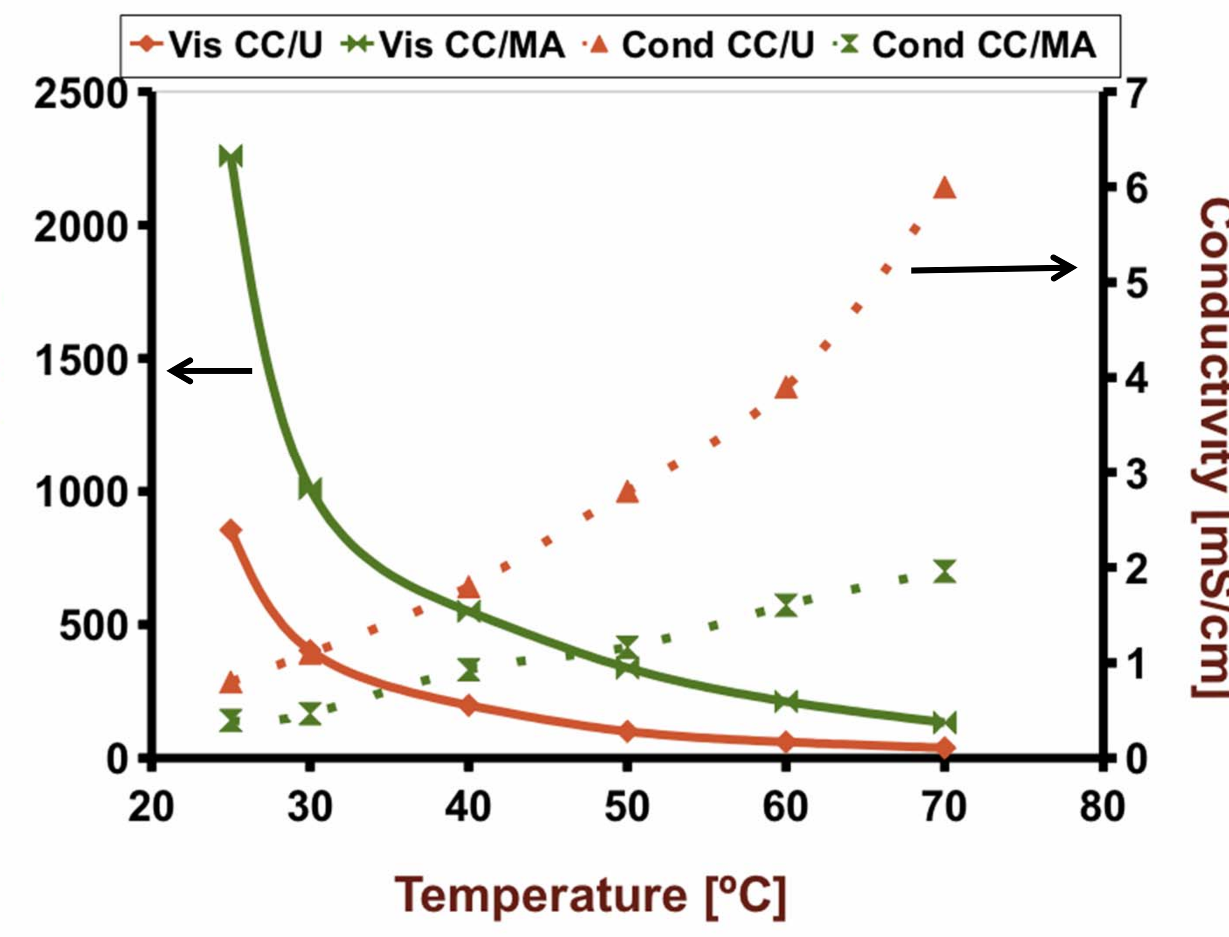
A.P. Abbott, et al., Journal of the American Chemical Society, *9 (126)*, p. 29 (2004)

Comparison between CC/U and CC/MA DES

Properties	Choline Chloride/Urea	Choline Chloride/Malonic Acid
Eutectic Temperature (°C)	12	10
Solubility of CuO (ppm)	~5	~14000
Solubility of Cu_2O (ppm)	~200	~18000
Mechanism of Metal Oxide Removal	Complex formation $[MClO.(Urea)]^-$	Chlorometalate formation MCl_x^-
Viscosity at 25°C (cP)	855	2260
Conductivity ($mScm^{-1}$)	0.8	0.4
Water Soluble	Yes	Yes
	CC U	CC MA

A.P. Abbott, et al., J. Chem. Eng Data, 51, p.1280-1282 (2006)

Conductivity and Viscosity of DES Systems at Different Temperatures



For CC/MA: high viscosity (> 1000 cP at RT) but reduces to < 100 cP at 70ºC for CC/MA

Comparison: Viscosity of 98 % H_2SO_4 is ~ 30 cP at RT

- **Good conductivity at 25ºC** (~ 1 $mScm^{-1}$ for CC/U, ~ 0.4 $mScm^{-1}$ for CC/MA) [Comparison: Conductivity of 250:1 dilute HF is ~ 5.2 $mScm^{-1}$]
- **Conductivity increases with temperature** (6 $mScm^{-1}$ for CC/U, 2 $mScm^{-1}$ for CC/MA @ 70ºC)

Objectives

OVERALL OBJECTIVE

- **Develop cleaning formulations based on electrically conductive deep eutectic solvents (DES) to replace traditional organic solvent based formulations for BEOL cleaning**

SPECIFIC OBJECTIVE FOR THE CURRENT CONTRACT YEAR

- **Extend the work on removal of post etch residues (PER) formed on copper using choline chloride/urea (CC/U) DES**

- **Explore the use of choline chloride/malonic acid (CC/MA) DES in PER removal and compare with CC/U DES which was discussed in 2010 SRC Annual Review**

ESH Metrics and Impact

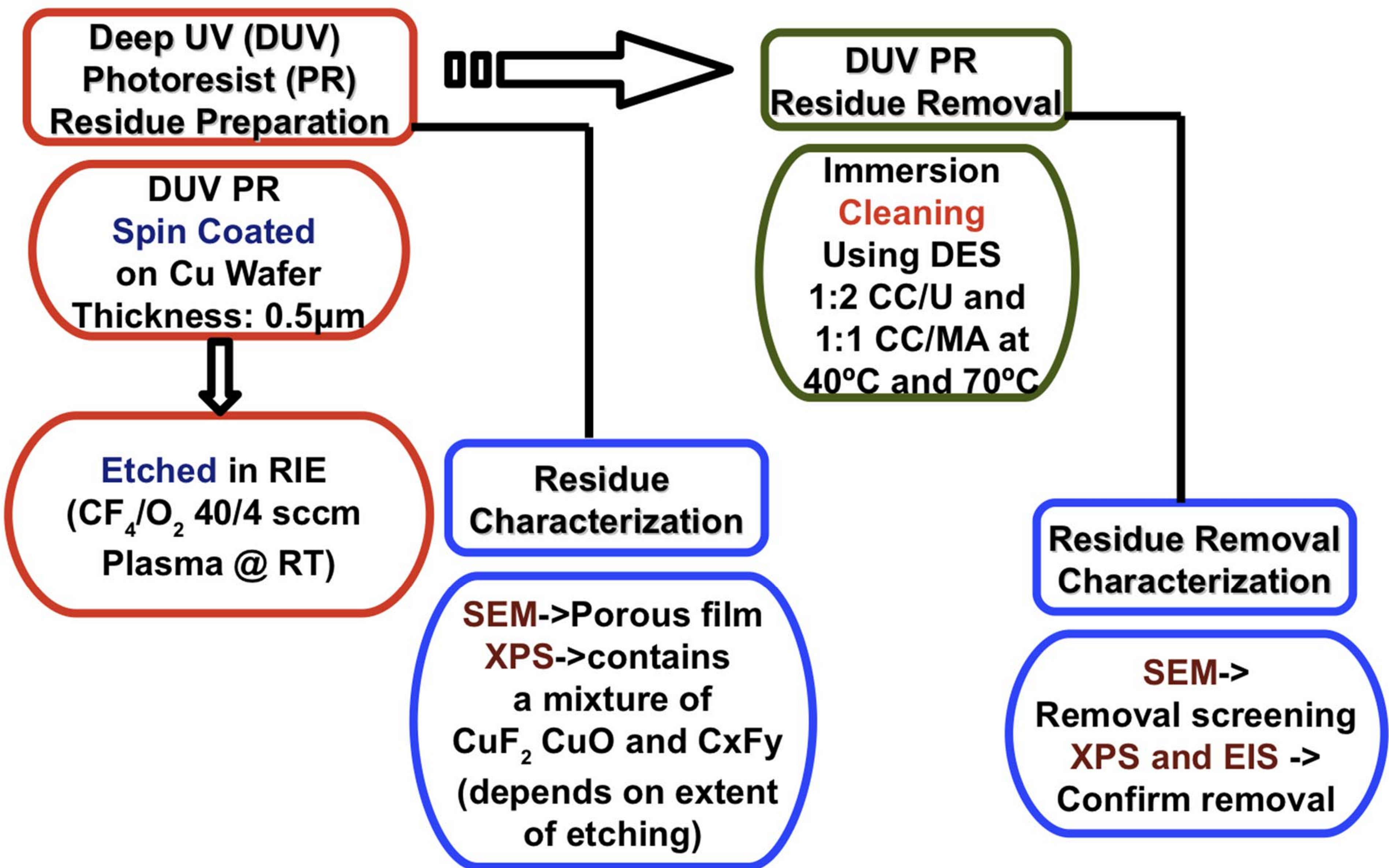
ESH objective: **Replacement of organic solvents from BEOL cleaning formulations which generate a waste stream that is difficult to treat**

Solution components	Wt % in typical formulations	Formulation used in this study
Traditional organic Solvent	> 60%	Two benign compounds 100%
Water	< 40%	0%
Fluoride	~ 1-2%	0%

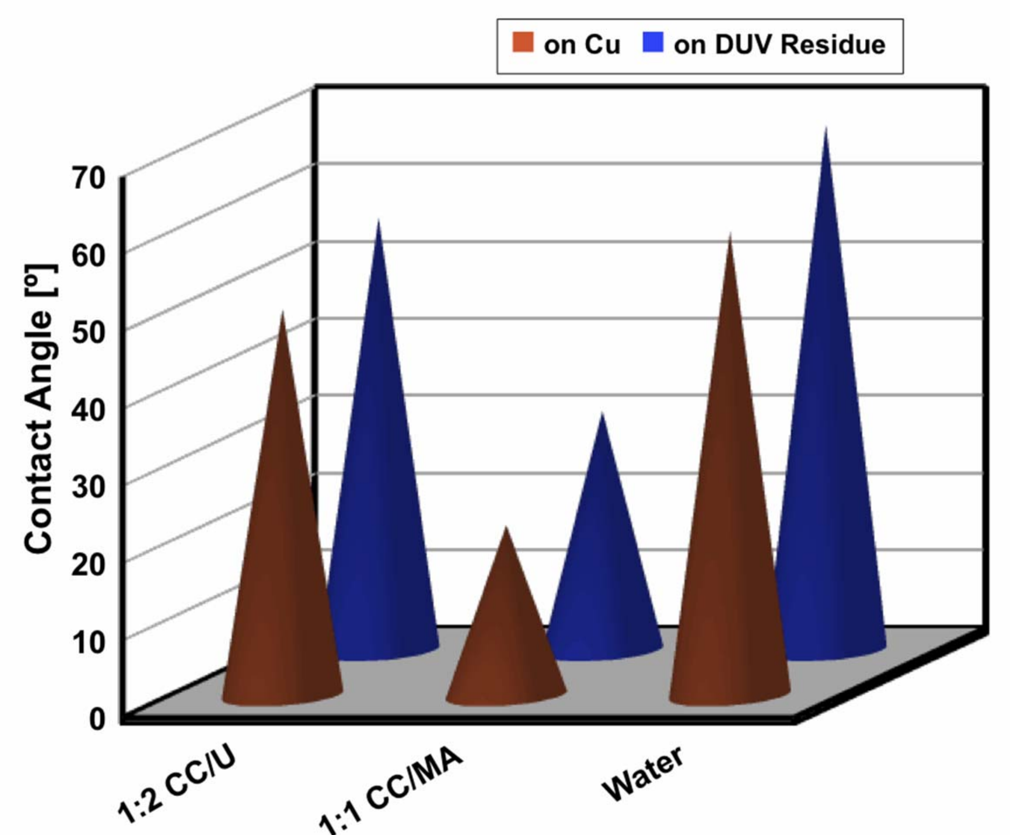
Ingredients	LD_{50} (Oral Rat) mg/kg
Urea	**8471**
Choline Chloride	**5000**
Malonic Acid	**1310**

Components	Vapor Pressure (@20^{0}C) mm Hg
DES Components:	
Choline Chloride (Solid)	**4.93 E-10 @25^{0}C**
Urea (Solid)	**6.75 E-3**
Malonic Acid (Solid)	**NA**
Conventional Solvents:	
DMSO	**0.42**
N-Methyl Pyrrolidone	**0.29**
Sulfolane	**0.01**

Experimental Approach



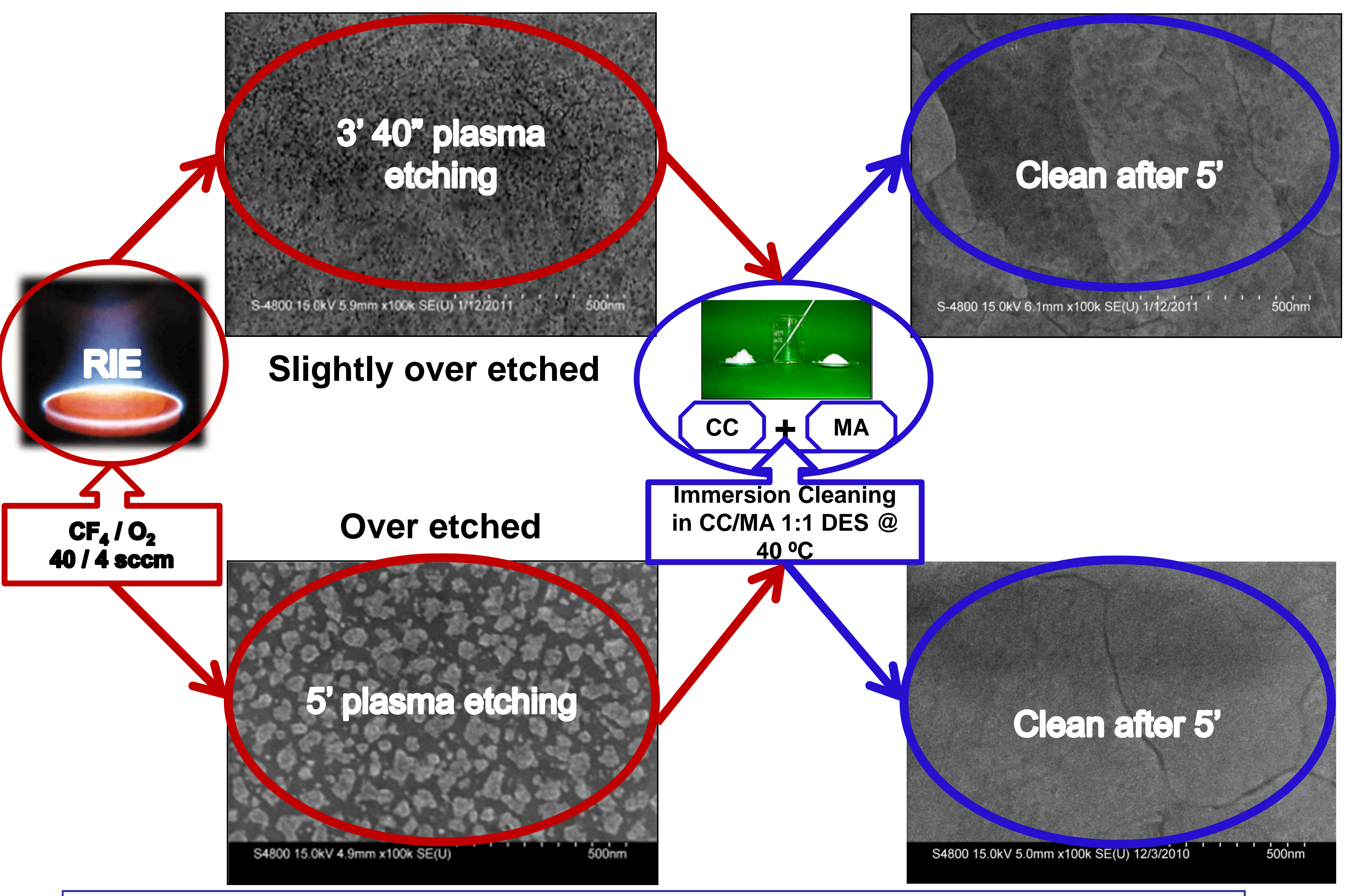
Wettability of Cu and PER Film by DES and Water



- PER (DUV PR plasma etched 3'40") is hydrophobic
- CC/U contact angle on copper and residue film comparable to water
- CC/MA showed better wetting than CC/U

Surface Tension mN m^{-1}	Water	CC/MA	CC/U
	72	66	50

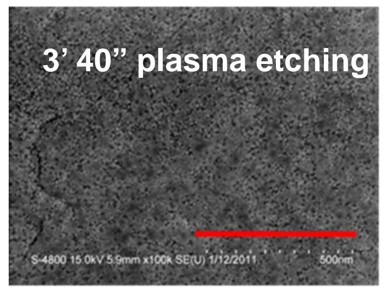
DUV PER Removal Using CC/MA - SEM Characterization



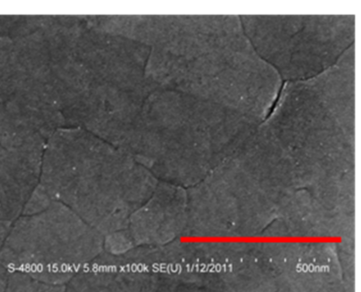
DUV PER Removal Using CC/U - SEM Characterization

Residue removal using 1:2 CC/U at 40ºC

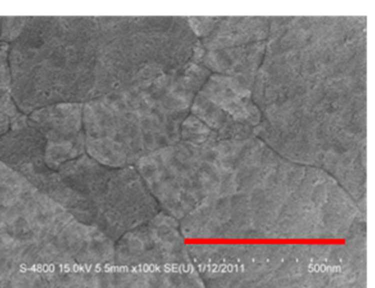
0.5 µm



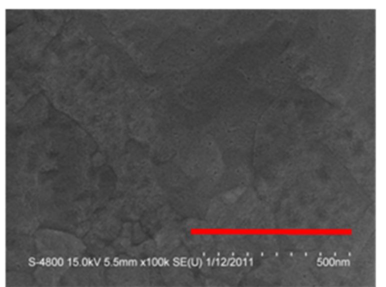
0 min



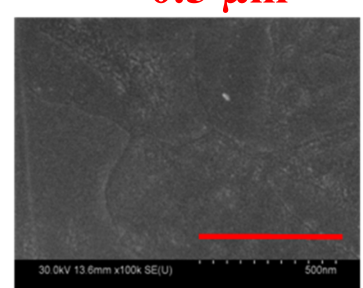
5 min



10 min



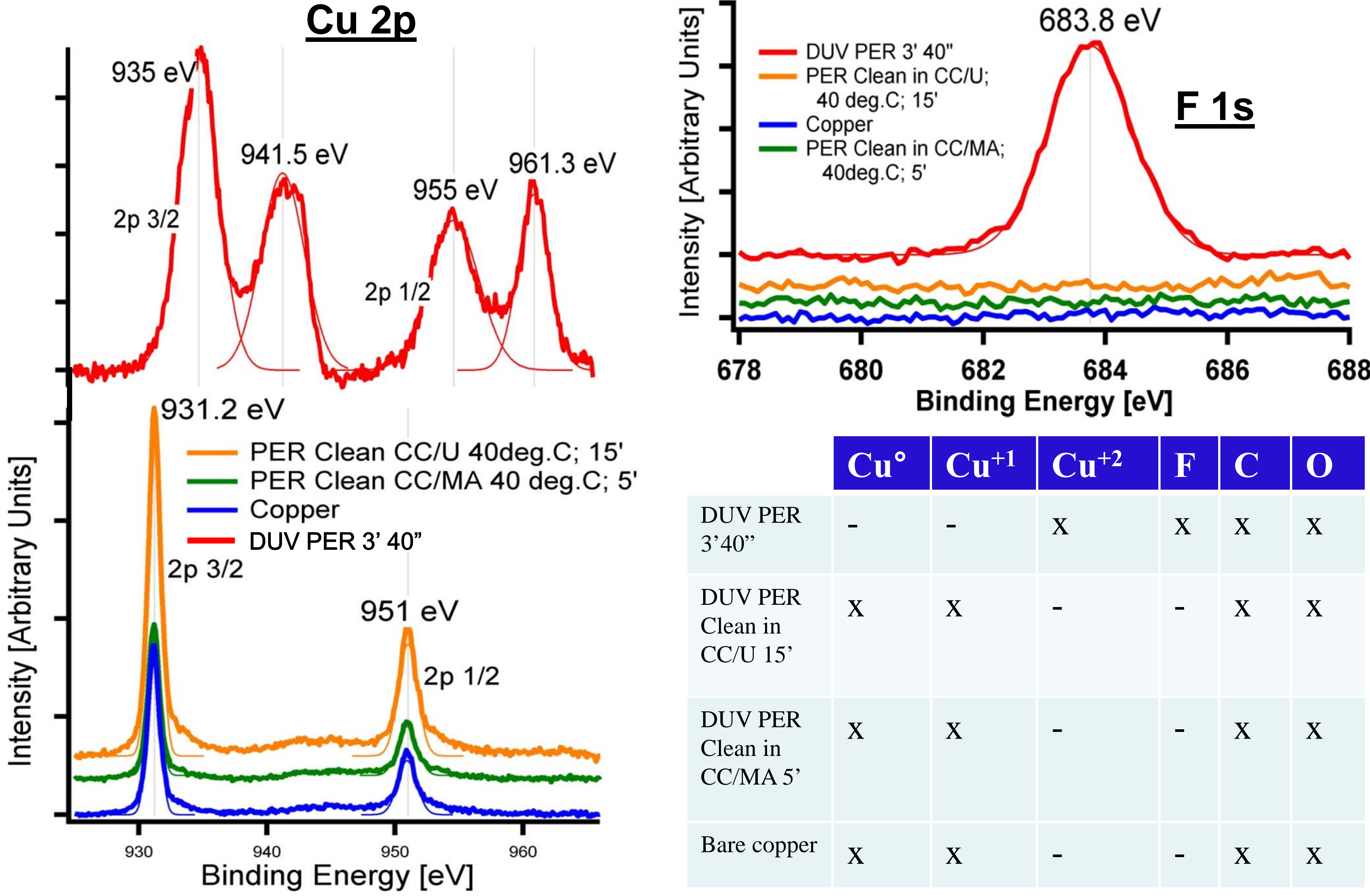
15 min



Plasma treated Cu exposed to DES, 5min

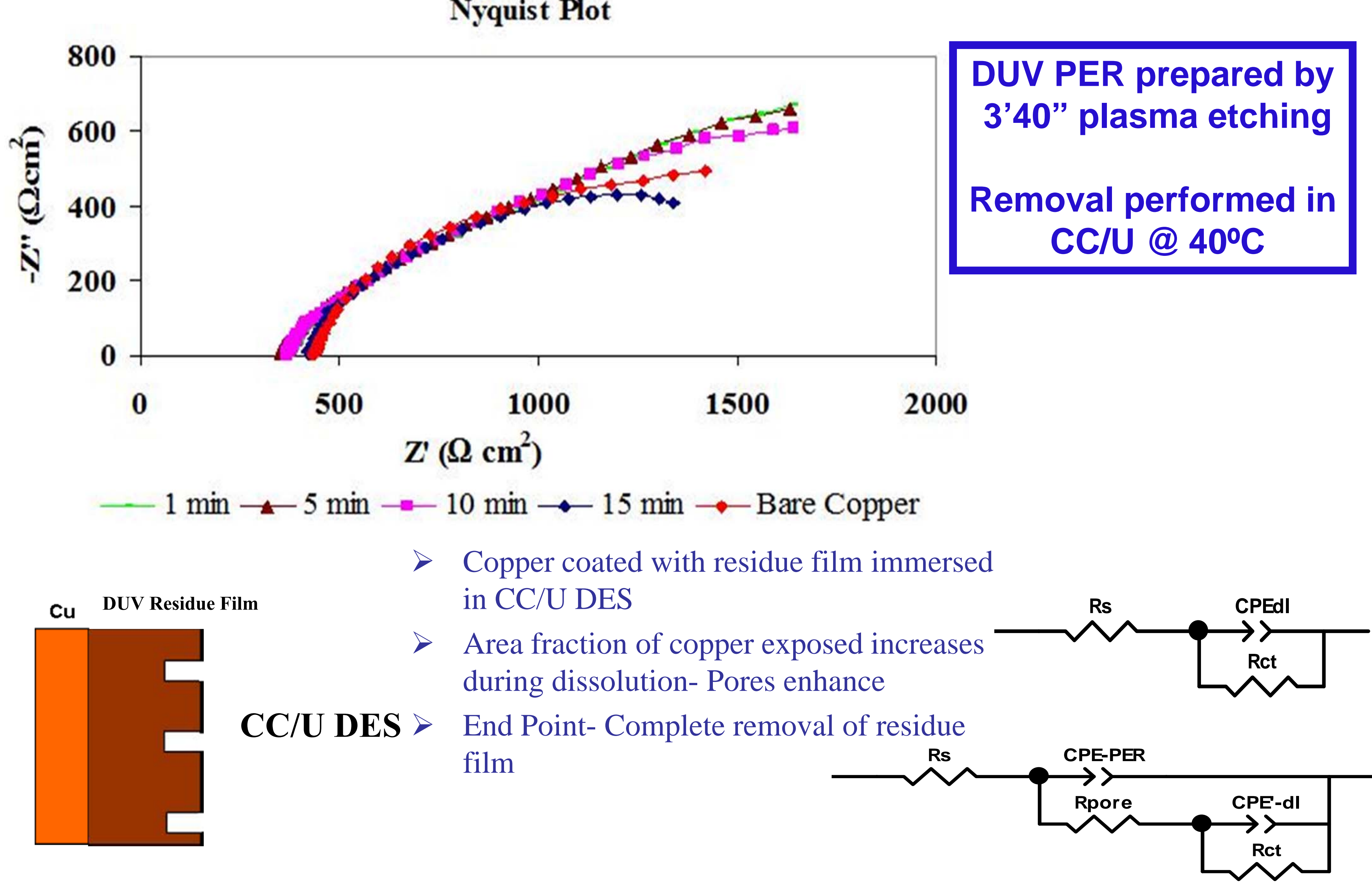
Plasma (CF_4/O_2) etching time	DUV PER Removal Time [minutes]			
	CC/U		CC/MA	
	@ 40 ºC	@ 70 ºC	@ 40 ºC	@ 70 ºC
3' 40"	15	10	5	5
5'			5	5
8'	30	20		

DUV PER Removal Using DES Systems - XPS Characterization

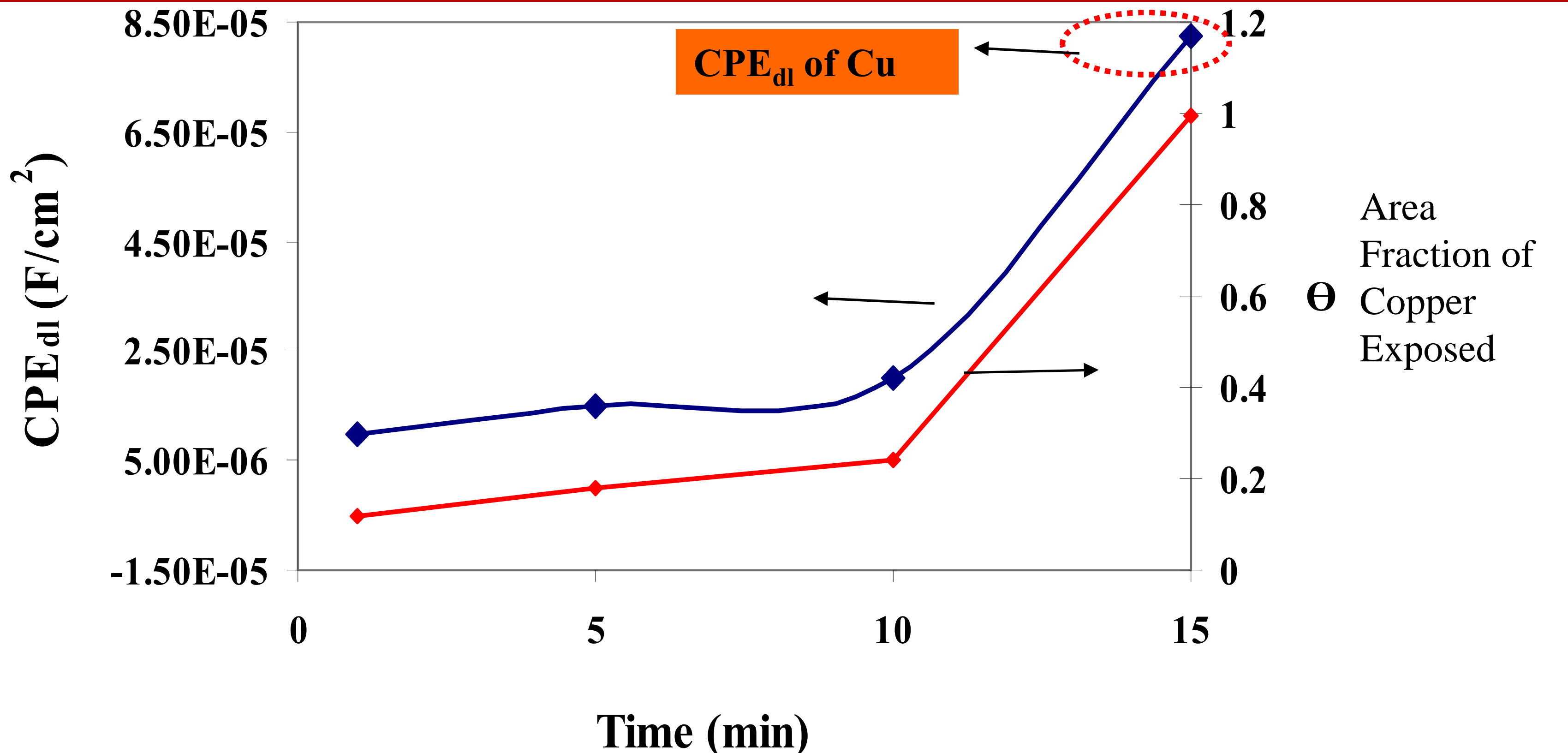


	Cu°	Cu^{+1}	Cu^{+2}	F	C	O
DUV PER 3'40"	-	-	X	X	X	X
DUV PER Clean in CC/U 15'	X	X	-	-	X	X
DUV PER Clean in CC/MA 5'	X	X	-	-	X	X
Bare copper	X	X	-	-	X	X

PER Removal Confirmation Using Electrochemical Impedance Spectroscopy (EIS)



EIS Electrochemical Parameters – Confirmation of PER Removal



- Impedance data is fitted to the equivalent circuit to extract the electrical parameters
- The parameter values obtained for copper coated with PER film match that of bare copper after complete removal
- Also, the ratio of double layer capacitance (constant phase element- CPE) CPEdl (residue)/ CPEdl (Cu) approaches one during removal
- EIS studies show complete removal in 15 min
- This agrees well with SEM and XPS characterization for residue removal

Conclusions

- **DES CC/MA and CC/U at 40 and 70ºC are *effective in removing DUV PER***
- **CC/MA DES System *cleans and wets DUV PER faster* than CC/U DES**
- **PER removal rate is slightly slower in DES than in conventional formulations but *DES systems are more environmentally benign***

Summary

Tasks Proposed Last Year	Accomplished Tasks	Work In Progress
Refine CC/U DES	• 2:1 DES @ 40 and 70°C effectively removed residue film on copper • Electrochemical impedance spectroscopy study of residue removal	• Removal of under etched residue film on copper
Explore CC/MA DES	• 1:1 DES @ 40 and 70°C removed residue faster than CC/U • Better wetting characteristic than CC/U	• Removal of under etched residue film on copper • Electrochemical impedance spectroscopy study of residue removal
Viscosity reduction of DES	• Viscosity reduction achieved by addition of polar solvents like water	• Study the effect of water addition to DES on copper corrosion rate
Spin cleaning	• -	• Study of reduction of cleaning time

Industrial Interactions and Technology Transfer

- Teleconference with Dr. Kanwal Singh and Bob Turkot, Intel, to discuss results and seek advice on future direction
  - Investigation on the use of DES for crust and photoresist removal from Intel patterned structures

- Collaboration with IMEC in testing the DES formulations for residue removal on low-k structures

- **Invention disclosure filed on September 28, 2010 with the University of Arizona**
  - **Patent to be filed by SRC**

Acknowledgements

- Dr. Kanwal Singh and Bob Turkot, Intel, SRC/GRC Industry Liaison

- Dr. Le Quoc Toan, IMEC

- Dr. Manish Keswani, Assistant Research Professor, Materials Science and Engineering, University of Arizona

Publications, Presentations, and Recognitions/Awards

Publication

- D. P. R. Thanu and S. Raghavan, "Benign Deep Eutectic Solvents (DES) for Replacement of Organic Solvents Based Cleaning Formulations in Back End of Line Cleaning", TECHCON Proceedings, p.1-4, Sep 15, Austin, TX (2010)

Presentations

- D. P. R. Thanu and S. Raghavan, "Benign Deep Eutectic Solvents (DES) for Replacement of Organic Solvents Based Cleaning Formulations in Back End of Line Cleaning", TECHCON Oral Presentation and Poster, Sep 15, Austin, TX (2010)
- S.Raghavan and D. P. R. Thanu, " Improvement of ESH Impacts of BEOL Formulations Using Ionic Liquids to Replace Traditional Solvents", IMEC, Sep 2010, Leuven, Belgium
- D. P. R. Thanu and S. Raghavan, "Liquid Mixtures of Urea and Choline Chloride for Use in BEOL Cleaning", SRC Teleseminar, Jan 27, 2011, Tucson, Arizona
- J. Taubert, D. P. R. Thanu, M. Keswani and S. Raghavan, " Back End of Line Cleaning of Post Etch Residues using Deep Eutectic Solvents (DES)", SPCC, SEMATECH, Austin, TX, March 2011
- J. Taubert and S. Raghavan, " Choline Chloride / Malonic Acid Deep Eutectic Solvent for Post Etch Residue Removal in BEOL Cleaning, submitted for presentation at 2011 TECHCON

Future Plans

Next Year Plans

- **Removal study of post etch residues formed on copper and low-k during etching with CF_4/Ar plasma**

- **Work with Intel and IMEC to evaluate DES for residue removal on PR/low-k structures**

Long-term Plans

- **Develop a single step process of photoresist stripping and residue removal using DES**