Improvement of ESH Impact of Back End of Line (BEOL) Cleaning Formulations Using Ionic Liquids to Replace Traditional Solvents

(*Task Number: 425.034*)

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  (now working for Intel in Chandler)

Cost Share (other than core ERC funding):

- **Patterned wafers (~$10k) from IMEC and Intel**

Objectives

Overall Objective

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

Specific objectives for work carried out during 2009-2011

- **Develop choline chloride/urea (CC/U) and choline chloride/malonic acid (CC/MA) DES formulations for post etch residues (PER)**
- **Study the effect of PER composition on residue removal in choline chloride/malonic acid (CC/MA) DES**
- **Explore the use of CC/MA formulation to strip PER and photoresist in one step**

ESH Metrics and Impact

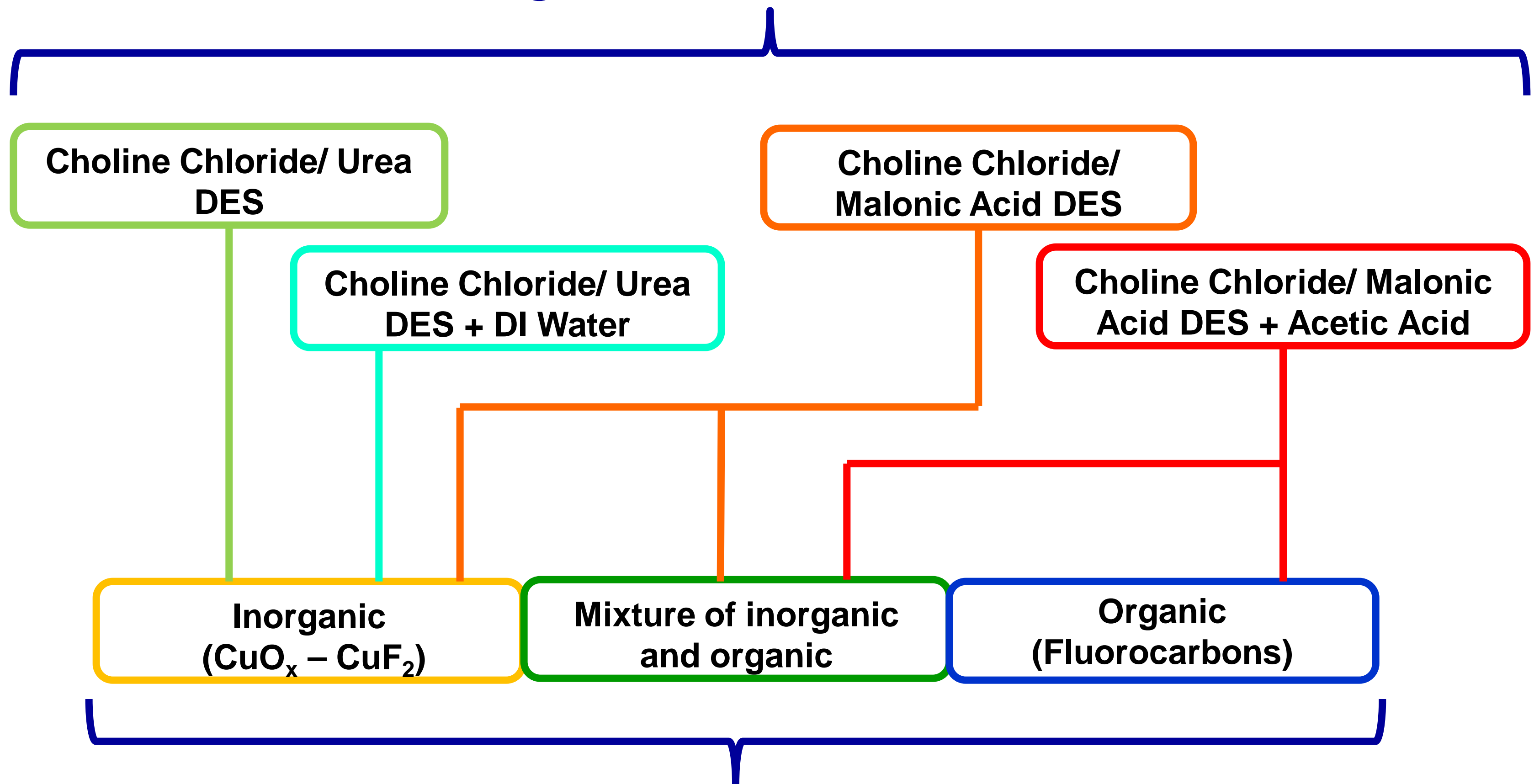
Replacement of organic solvents from BEOL cleaning formulations which generate a waste stream that is difficult to treat

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

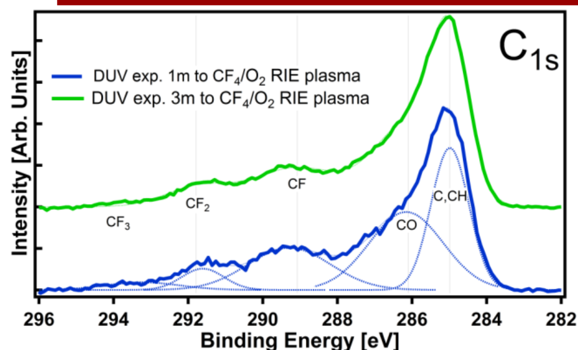
Ingredients	LD_{50} (Oral Rat) mg/kg
Choline Chloride	**5000**
Urea	**8471**
Malonic Acid	**1310**

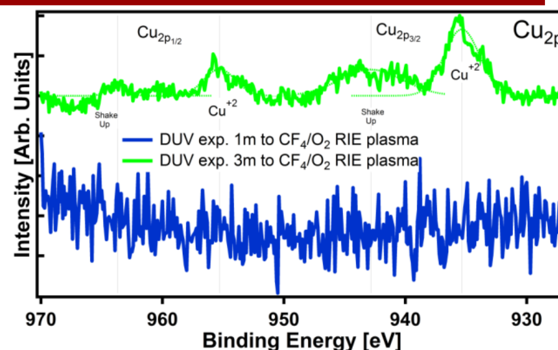
Components	Vapor Pressure (@20^{0}C) mm Hg
DES Components:	
Choline Chloride (Solid)	**4.93 E-10 @25°C**
Urea (Solid)	**6.75 E-3**
Malonic Acid (Solid)	**NA**
Conventional Solvents:	
DMSO	**0.42**
N-Methyl Pyrrolidone	**0.29**
Sulfolane	**0.01**

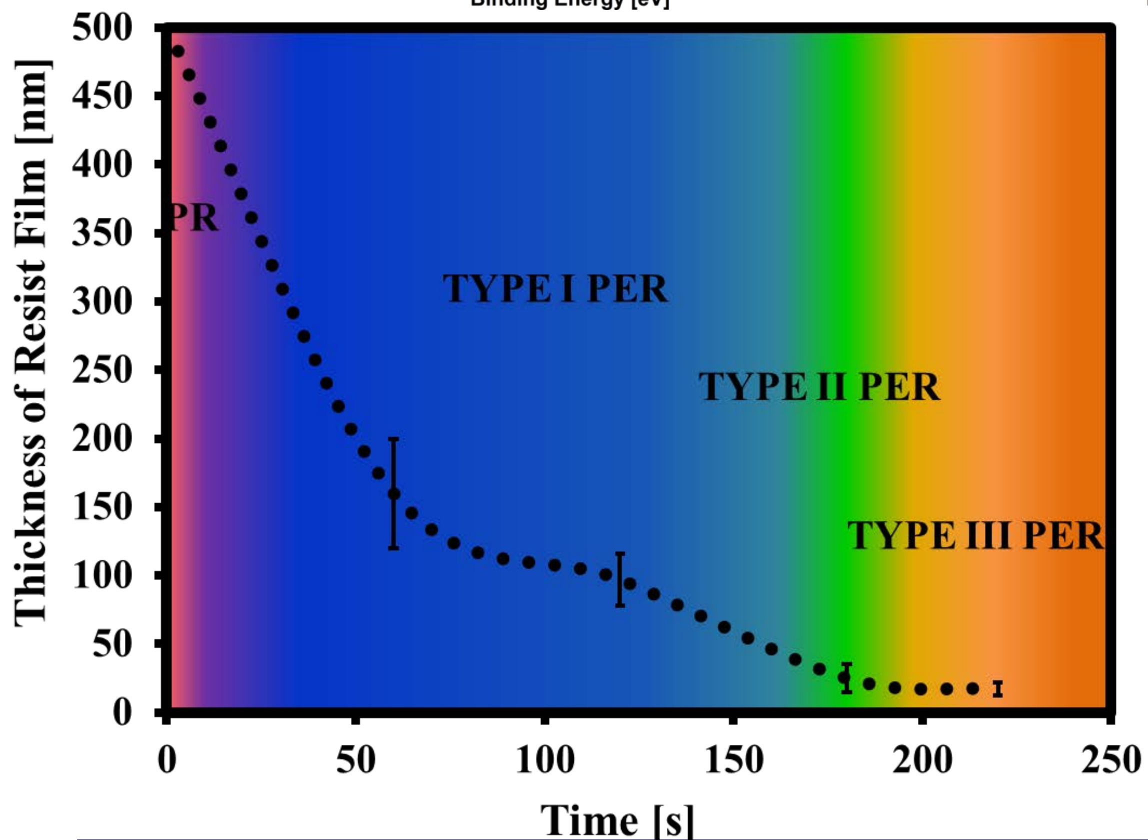
Method of Approach



Etching of DUV PR (0.5 μm film on Cu) In CF_4/O_2 Plasma: PER Evolution as a Function of Etch Time







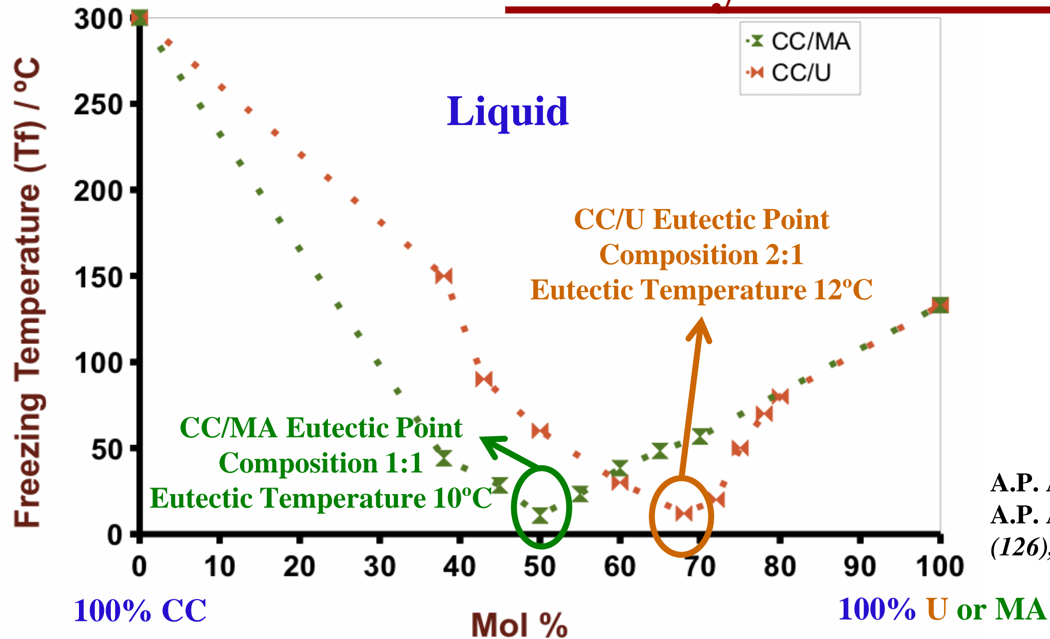
PR:
DUV Photoresist

Type I PER:
Organic compounds generated during etching DUV PR

Type II PER:
Mixture of organic and Cu based inorganic compounds

Type III PER:
Cu based Inorganic compounds

DES Systems Investigated



Deep eutectic solvent (DES) is a mixture of two chemicals, which forms an eutectic at a temperature much lower than the melting point of the individual components

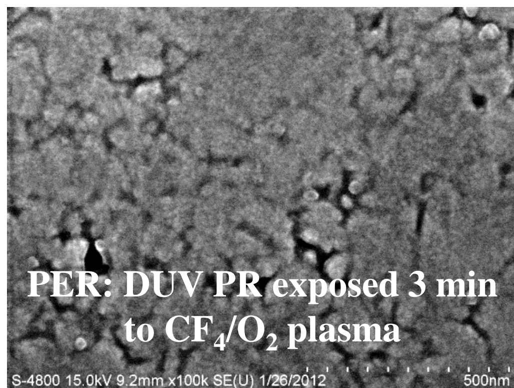
A.P. Abbott, et al., *Chemical Communications*, p. 70-71 (2003)
A.P. Abbott, et al., Journal of the American Chemical Society, *9 (126)*, p. 29 (2004)

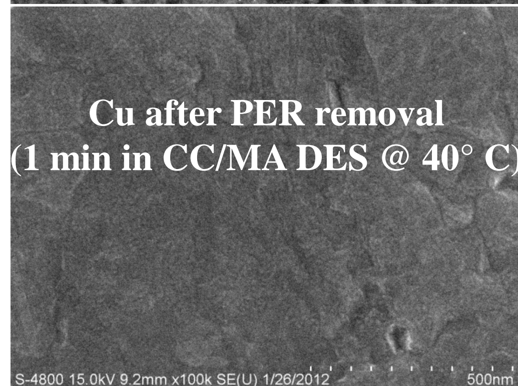
Choline Chloride/Urea	Choline Chloride/Malonic Acid
➢ Slightly alkaline ➢ Water added to reduce viscosity ➢ Removal of Type I and Type II PER not very efficient ➢ Removal of Type III PER complete in 15 min ➢ Water addition does not affect removal rate of Type III PER	➢ Highly acidic ➢ Acetic acid added to reduce viscosity and attack resist ➢ Formulation effective in removal of Type II and III PER; removal complete in 1 min ➢ Acetic acid addition helps in the removal of photoresist

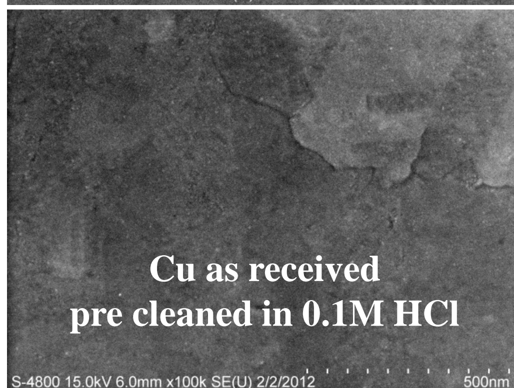
Removal of Types II and III PER in CC/MA and CC/U DES @ 40° C

Type II PER Thickness ~ 25 nm

Type III PER Thickness ~ 17 nm



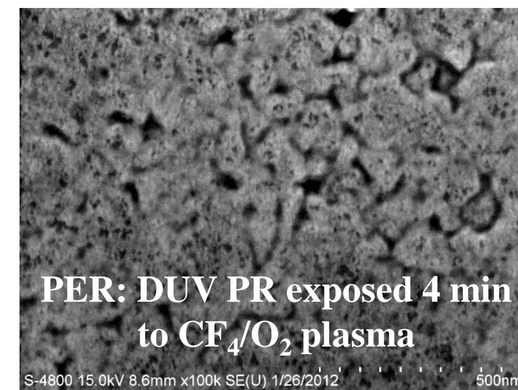


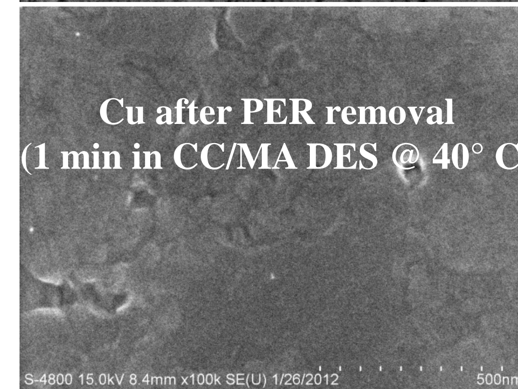


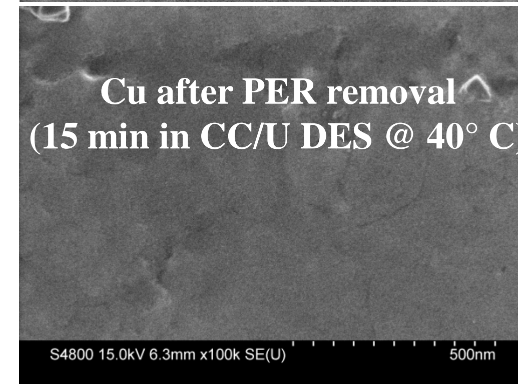
FE-SEM imaging results confirmed using Impedance measurements

Impedance value (at 1kHz) of Type II sample measured after 1min immersion in CC/MA is almost the same as that of a copper sample under similar conditions

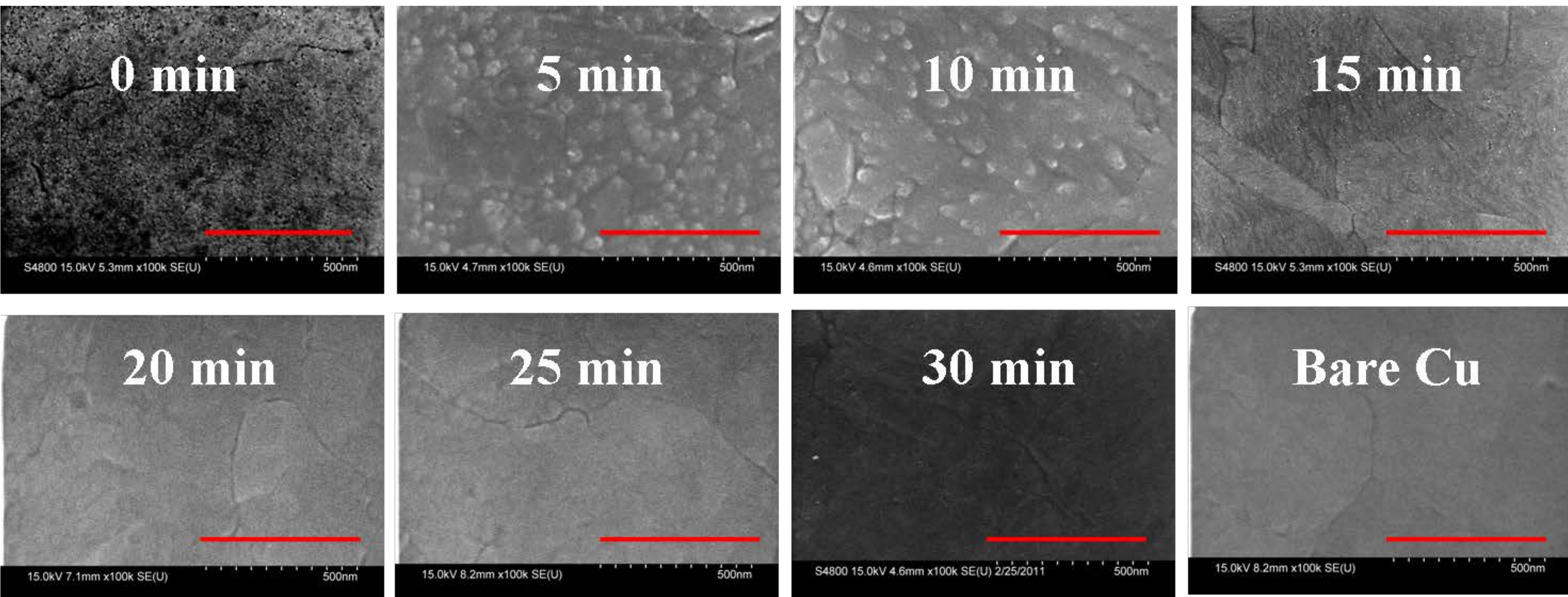
Electrochemical impedance spectroscopy results of Type III sample measured after 15min immersion in CC/U is almost the same as that of a copper sample under similar conditions







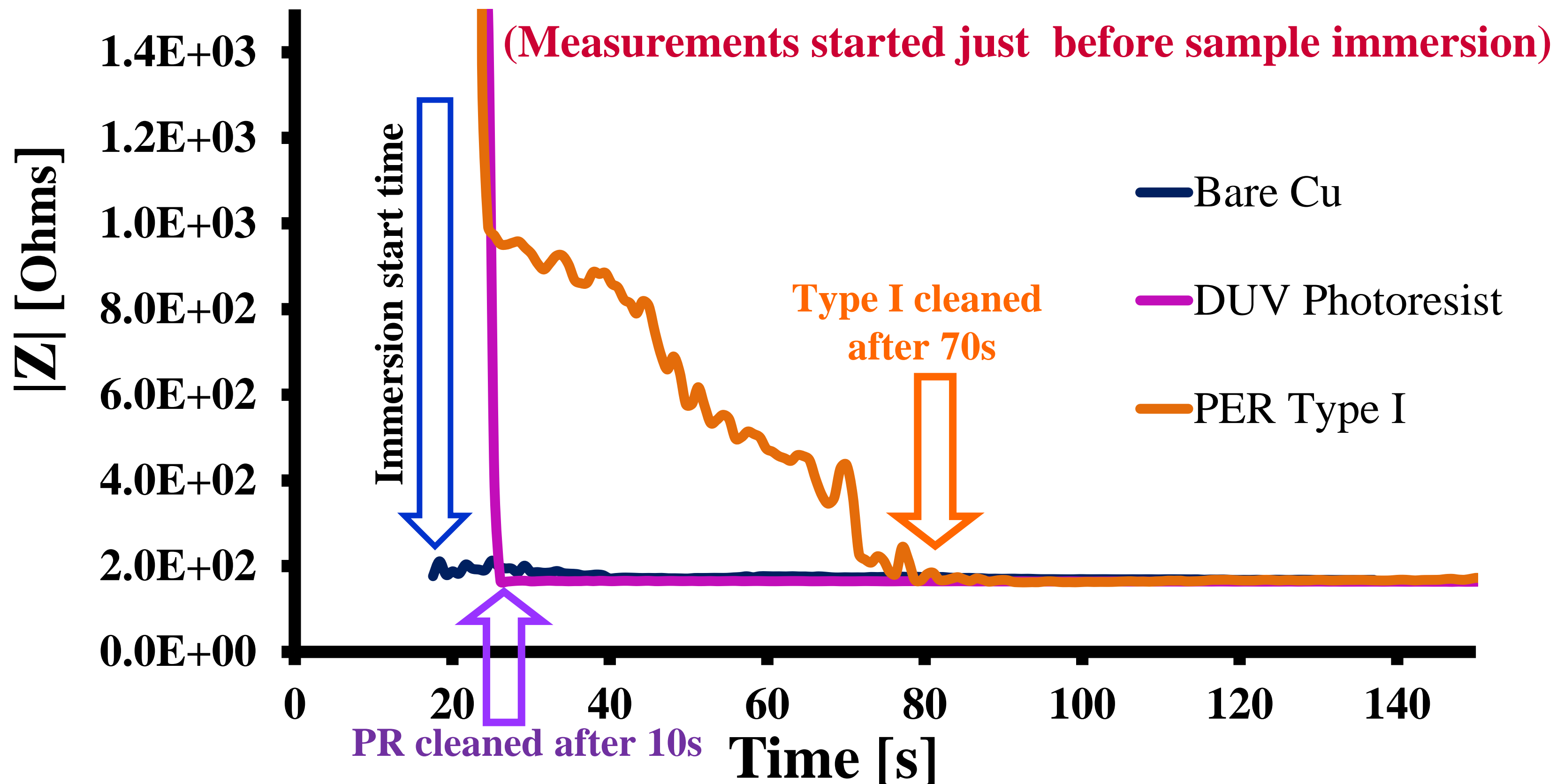
PER Type III Removal Using 90% W/CC/U at 20°C



- **Solutions investigated: 10 to 90 vol% W/CC/U at 20 to 40°C**
- **Residue removed by immersion cleaning with stirring and monitored using FE-SEM imaging**
- **Complete removal observed in *~15 min;* Removal rate is ~10 Å/min using 90%W/CC/U @ 20°C**
- **No corrosion of copper even after 30 min of immersion**

Removal of Photoresist and Type I PER Using Mixtures of CC/MA and Acetic Acid

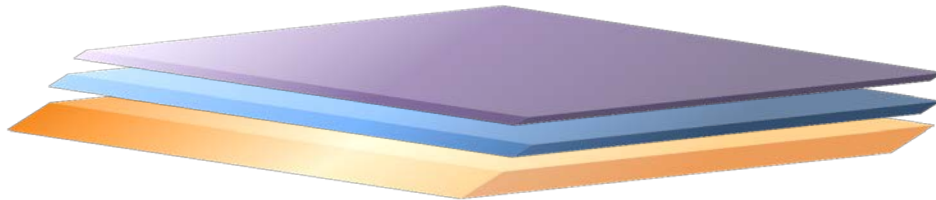
Semiconductor industry is very interested in BEOL cleaning formulations that are able to remove in one step both PER and PR remaining after patterning



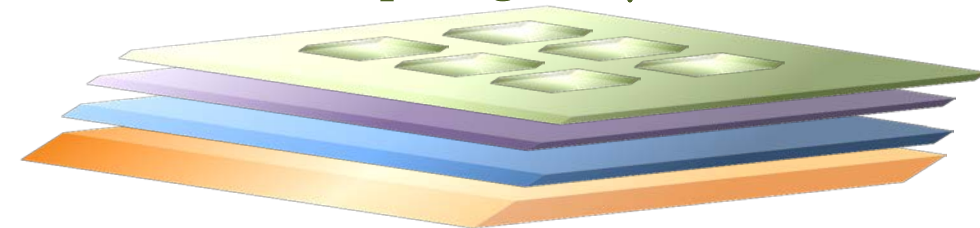
Fabrication of Patterned Wafers with Model PER

LITHOGRAPHY

- g-line Photoresist
- LTO SiO_2
- PVD Cu wafer



- Pattern transfer
  Mask made using
  μPG 101 (Heidelberg Instruments)
  Line/Spacing 7/12 μm



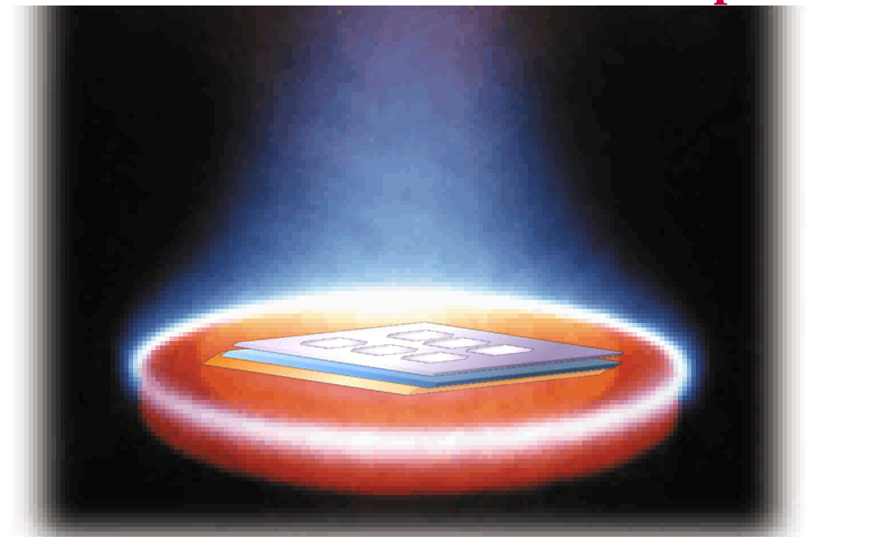
TWO STEP PLASMA ETCHING (RIE)*

CHF_3/Ar (40/4 sccm)
250W
50mT

Etch SiO_2

CHF_3/Ar (40/4 sccm)
100W
50mT

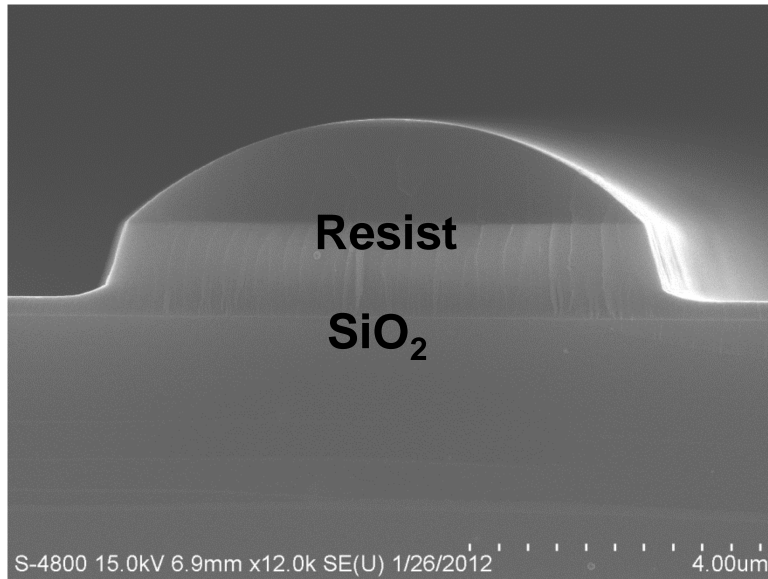
Fluorocarbon deposition

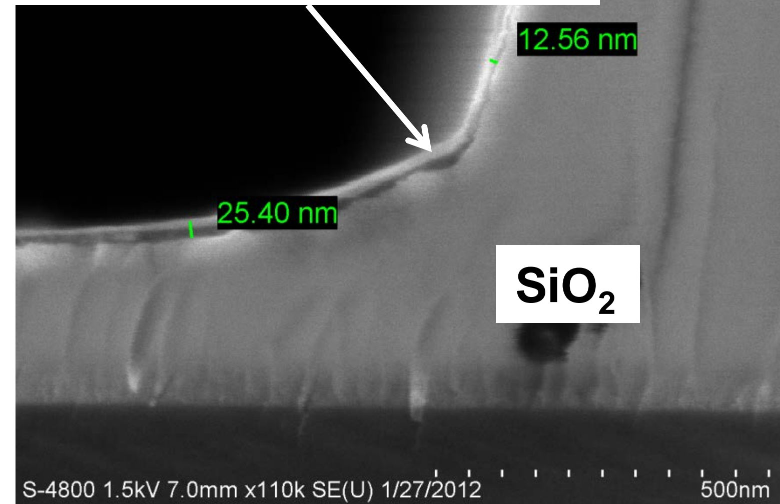


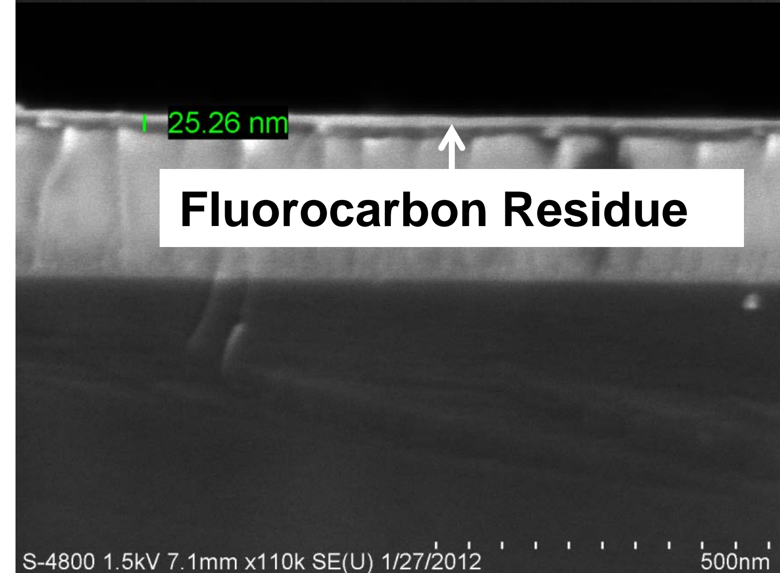
* Acknowledge discussions with Le Quoc Toan , IMEC

SEM Characterization of Patterned Wafers with Model PER

Fluorocarbon Based Residue Created by CHF_3/Ar Etching of SiO_2 Patterned with g-line Resist







Preliminary studies have shown that the residues containing complex fluorocarbons are difficult to remove with the current CC/MA DES formulation.
Pre-treatment with UV or UV/peroxide is being done to enhance attack by DES

COMPARISON OF DES BASED CLEANING FORMULATIONS

DUV PER Removal Rate [Å/min]				
Cleaning Formulation	**CC/U**	**W/CC/U**	**CC/MA**	**HAc/CC/MA**
Temperature [° C]	**40**	**40**	**40**	**30**
Etching Time [min] (using CF_4/O_2 plasma)				
0 (organic PR)	**-**	**-**	**-**	**Very high**
1' (PER Type I)	**-**	**-**	**-**	**Very high (>100 nm/min)**
3' (PER Type II)	**-**	**-**	**250**	**Very high**
4' (PER Type III)	**11**	**20**	**170**	**Very high**

Summary

BEOL CLEANING FORMULATIONS BASED ON DEEP EUTECTIC SOLVENT SYSTEMS ARE ENVIRONMENTALLY FRIENDLY ALTERNATIVES FOR TRADITIONAL CLEANING FORMULATIONS

- ***Addition of water (W) to CC/U or acetic acid (HAc) to CC/MA helps in reducing the viscosity of DES system and improves post etch residues removal rates***
- ***CC/U DES and W/CC/U DES remove inorganic PER***
- ***CC/MA DES removes inorganic and mixtures of organic and inorganic PER***
- ***HAc/CC/MA DES is a promising cleaning formulation to remove PER and PR***

Industrial Interactions and Technology Transfer

- Interactions with IMEC in testing the DES formulations for residue removal on patterned wafers
- Patent based on CC/U work filed on April 29, 2011 by SRC

Acknowledgements

- Dr. Kanwal Singh, Intel, SRC/GRC Industry Liaison
- Dr. QuocTon Le, IMEC
- Dr. Manish Keswani, Assistant Research Professor, Materials Science and Engineering, University of Arizona

Publications, Presentations, and Recognitions/Awards

Publications

- D. P. R. Thanu, S. Raghavan and M. Keswani, "Post Etch Residue Removal in Dilute HF Solutions", *Journal of The Electrochemical Society*, 158, H814-H820 (2011).
- D. P. R. Thanu, S. Raghavan and M. Keswani, "Liquid Mixtures of Urea and Choline Chloride for Use in Back End of Line Cleaning", *Electrochemical and Solid-State Letters*, 14, H358-H361 (2011).
- J. Taubert, M. Keswani and S. Raghavan, "Post Etch Residue Removal using Choline Chloride-Malonic Acid Deep Eutectic Solvent (DES)", *Microelectronic Engineering*, Published Online, Nov, 2011
- D. P. R. Thanu, S. Raghavan and M. Keswani, "Effect of Water Addition to Choline Chloride-Urea Deep Eutectic Solvent (DES) on the Removal of Post Etch Residues Formed on Copper", accepted for publication *in IEEE Transaction on Semiconductor Manufacturing*, Jan, 2012

Presentations

- S. Raghavan, J. Taubert, D. P. R. Thanu and M. Keswani, "Back End of Line Cleaning of Post Etch Residues Using Deep Eutectic Solvents", Sematech SPCC Conference, Austin, TX, March 2011.
- J. Taubert and S. Raghavan, "Effect of Composition of Post Etch Residues (PER) on their Removal in Choline Chloride Malonic Acid Deep Eutectic Solvent (DES) System", accepted for presentation in Sematech SPCC Conference, Austin, TX, March, 2012