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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Objectives

OVERALL OBJECTIVE

- **Develop cleaning formulations based on ionic liquids to replace traditional organic solvent based formulations for BEOL cleaning**

SPECIFIC OBJECTIVE FOR THE CURRENT CONTRACT YEAR

- **Investigate the use of deep eutectic solvents (DES) based on choline chloride and urea for the removal of post etch residues**

ESH Metrics and Impact

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

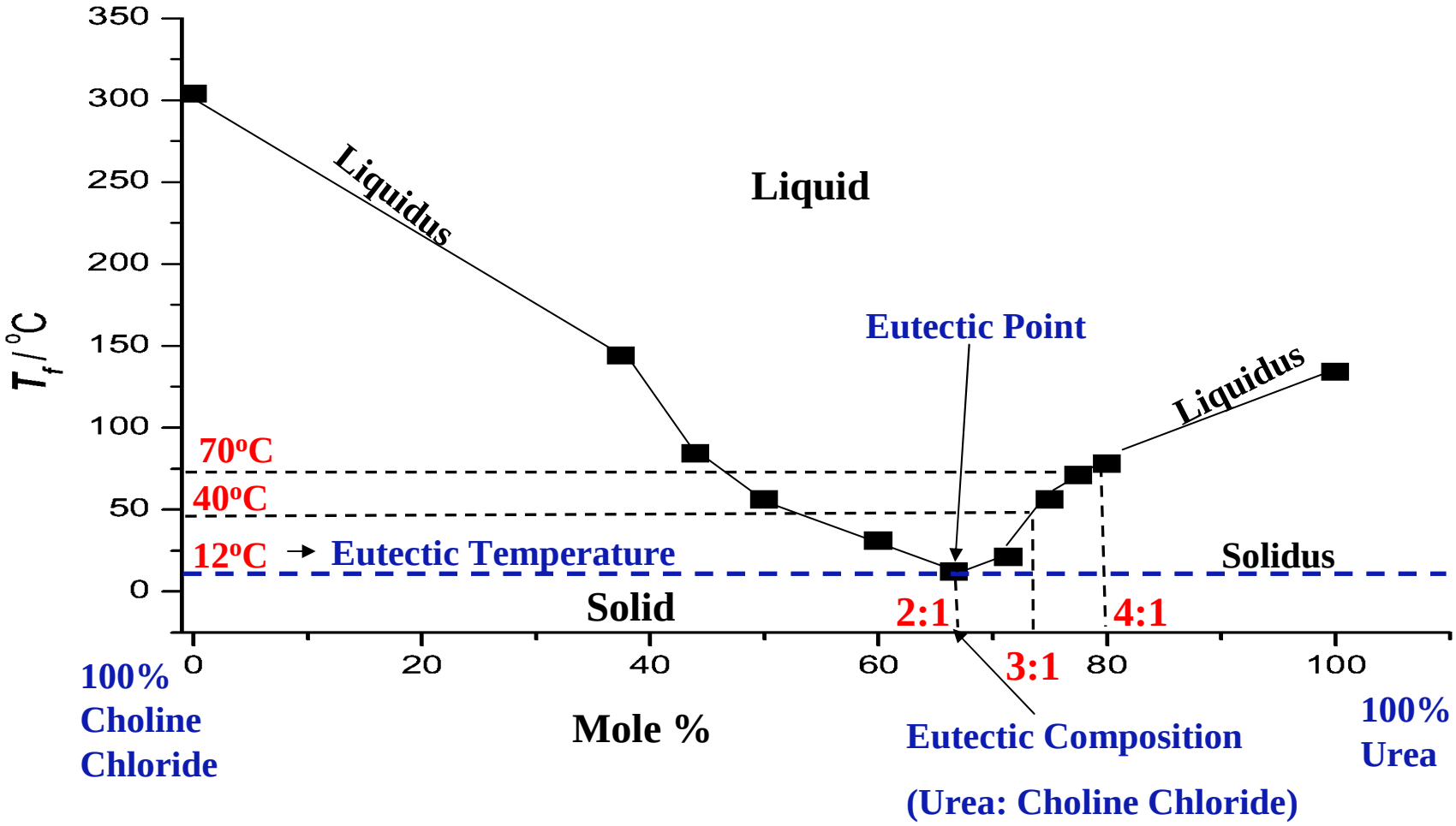
Solution components	**Weight % in typical formulations**	**Formulation used in this study**
Traditional organic Solvent	> 60%	Eutectic composition of two benign compounds 100%
Water	< 40%	0%
Fluoride	~ 1-2%	0%

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

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

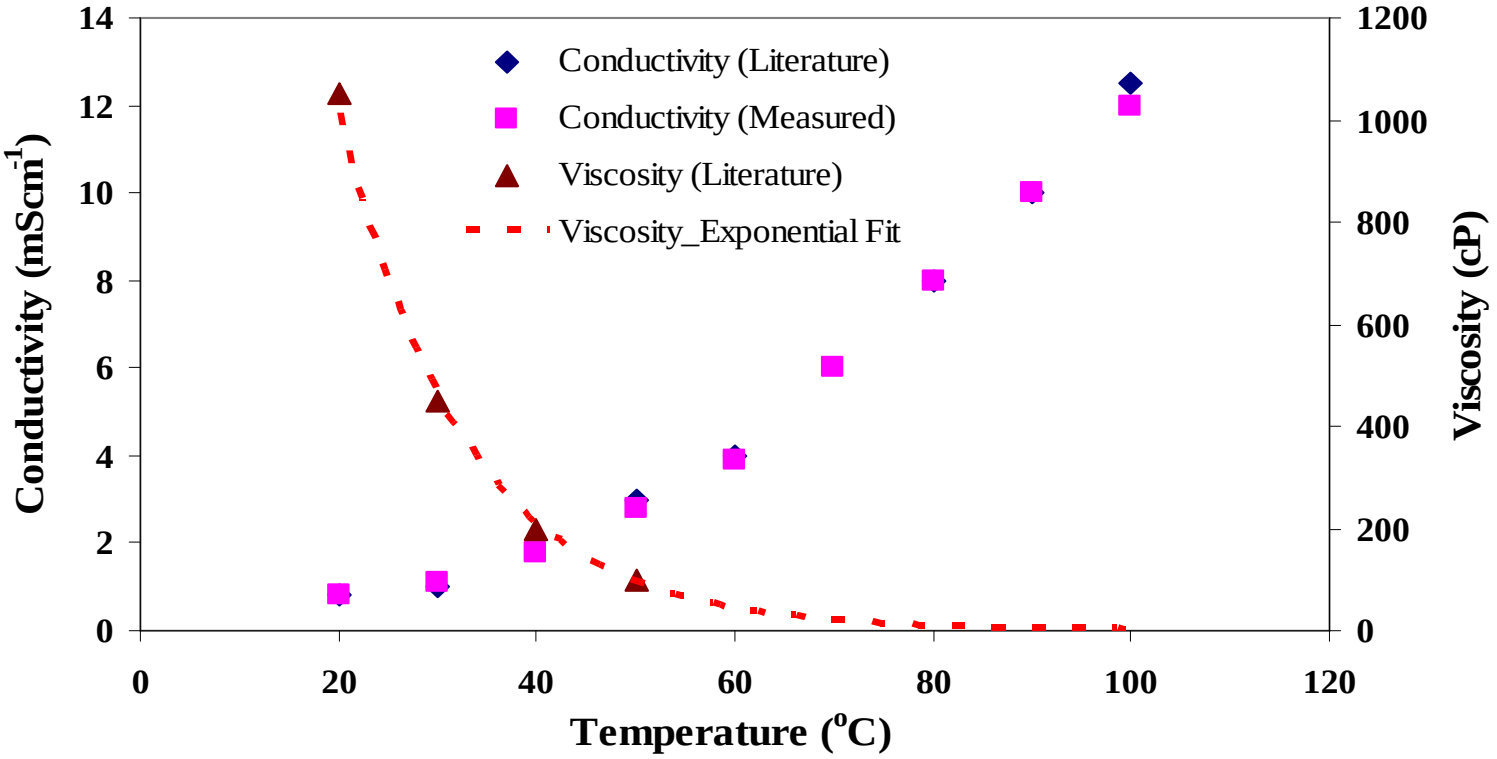
Deep Eutectic Solvents (DES)

(e.g.) Urea-Choline Chloride Binary Phase Diagram



- 2:1, 3:1 and 4:1 (urea:choline chloride) chosen for investigation

Conductivity and Viscosity of Urea:Choline Chloride (2:1) as a Function of Temperature



- Good conductivity (1mScm^{-1} @ 20°C), low vapor pressure and toxicity
- Conductivity increases with temperature (2mScm^{-1} @ 40°C, 6mScm^{-1} @70°C)
- High viscosity at room temperature and it decreases with increase in temperature
- Good solubility for copper oxides at elevated temperatures [1]

1. A. Abbott, et al., *Journal of Chemical Engineering Data*, Volume 51, p. 1280-1282 (2006)

Experimental Approach

Preparation of Residue Film

Photoresist coating:

- **Photoresist AZ 3312 (g line) spin coated on copper wafers to a thickness of 1.2µm at a spin speed of 4000 rpm for 30 seconds; Baking: 90°C for 90 seconds**

Photoresist ashing :

- **Ashed in Reactive Ion Etcher (RIE) tool at a rate of 1580 Å/min using CF_4/O_2 plasma at 50 mTorr pressure and 250W of plasma power; Ashing time: ~7min**

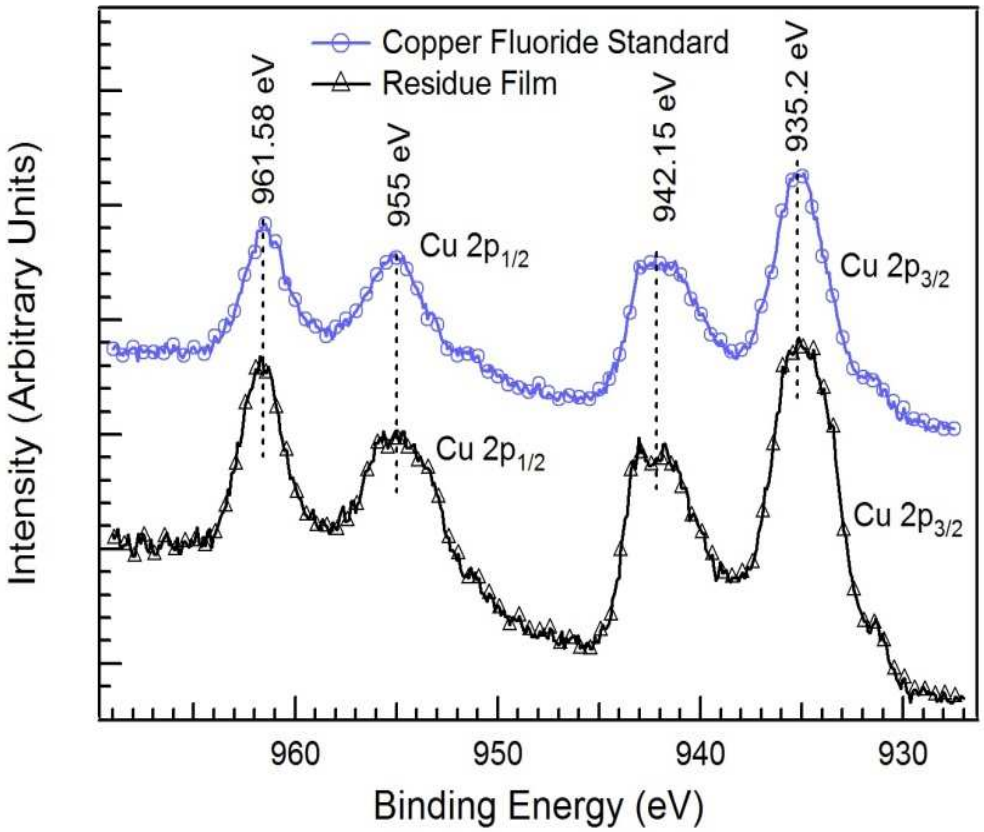
- **Thickness: ~30nm measured by Atomic Force Microscope step height measurements**

- **Contains mainly CuF_2 as determined from X-ray Photoelectron Spectroscopy (XPS)**

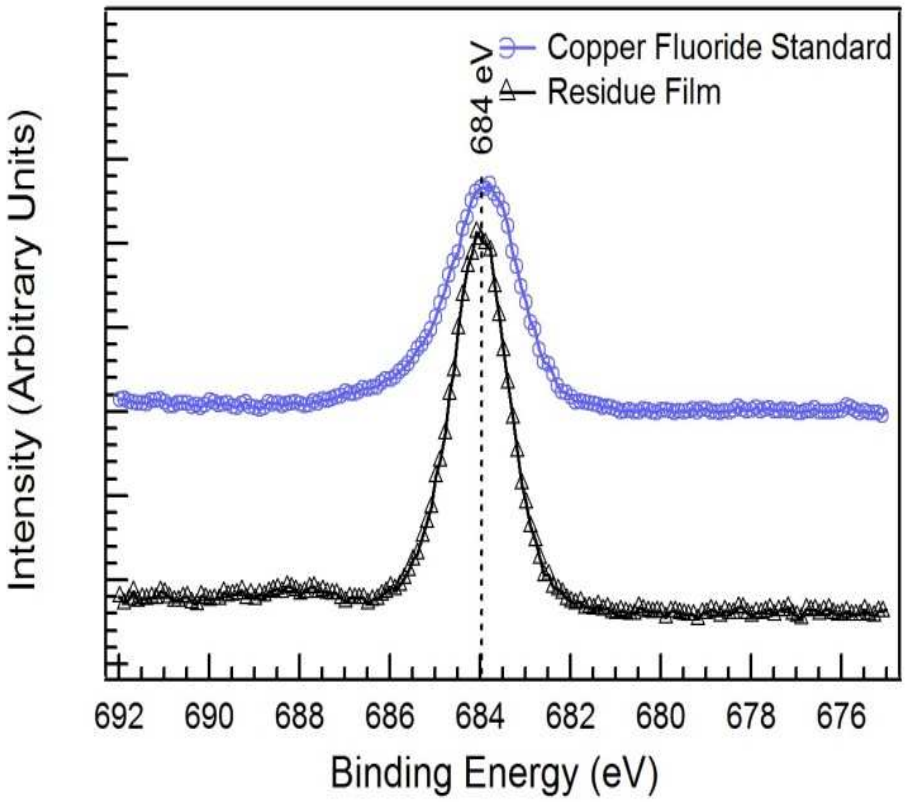
Methods

- **Residue removal investigated using Scanning Electron Microscopy (SEM) and confirmed using XPS and open circuit potential measurements**

Oxidation State and Bonding of Elements in Residue Film- Comparison with CuF_2 Standard



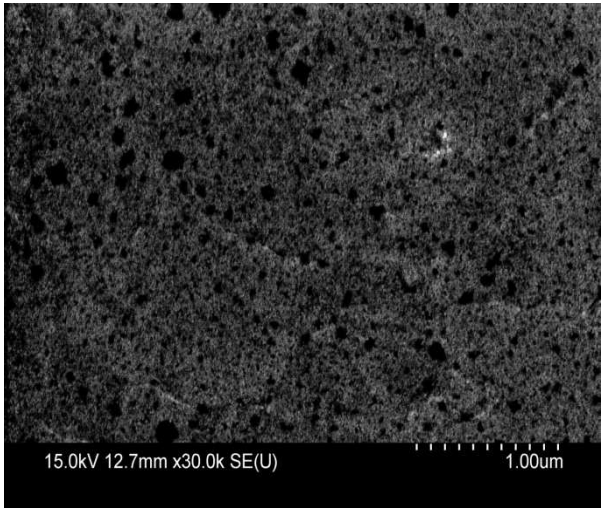
Cu 2p spectrum



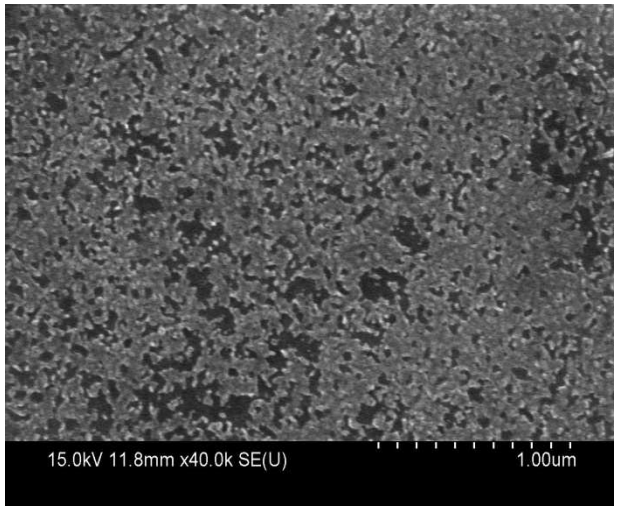
F 1s spectrum

- Copper exists in +2 oxidation state
- Residue film mainly contains CuF_2

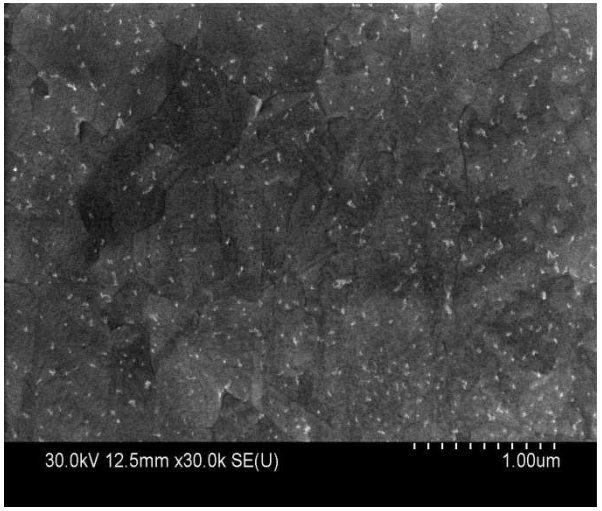
Residue Removal using 2:1 DES (Urea:Choline Chloride) at 40°C



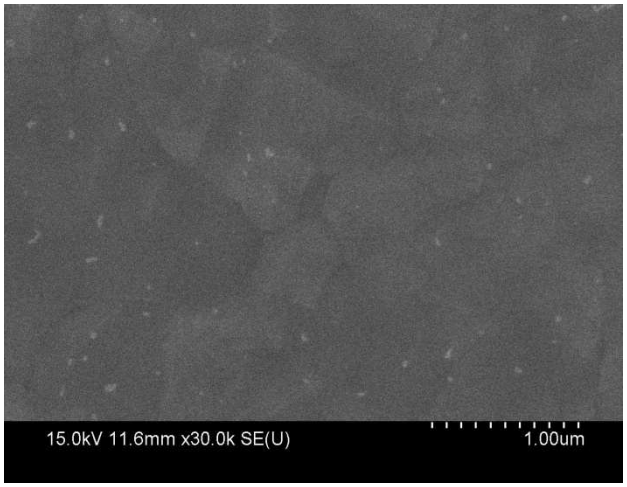
0 min



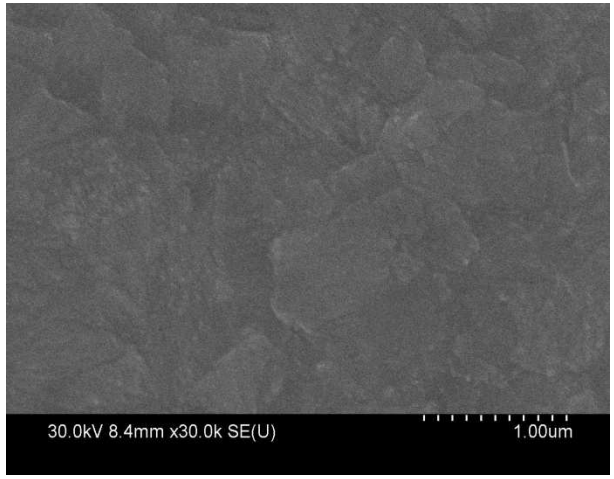
5 min



10 min



30 min

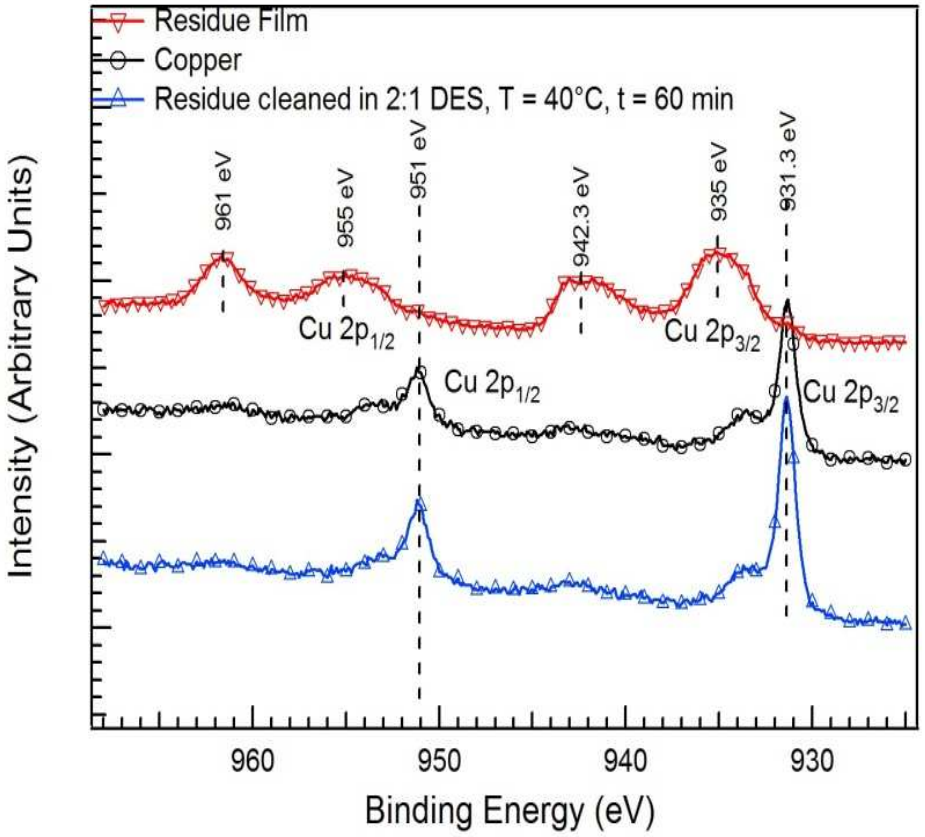


60 min

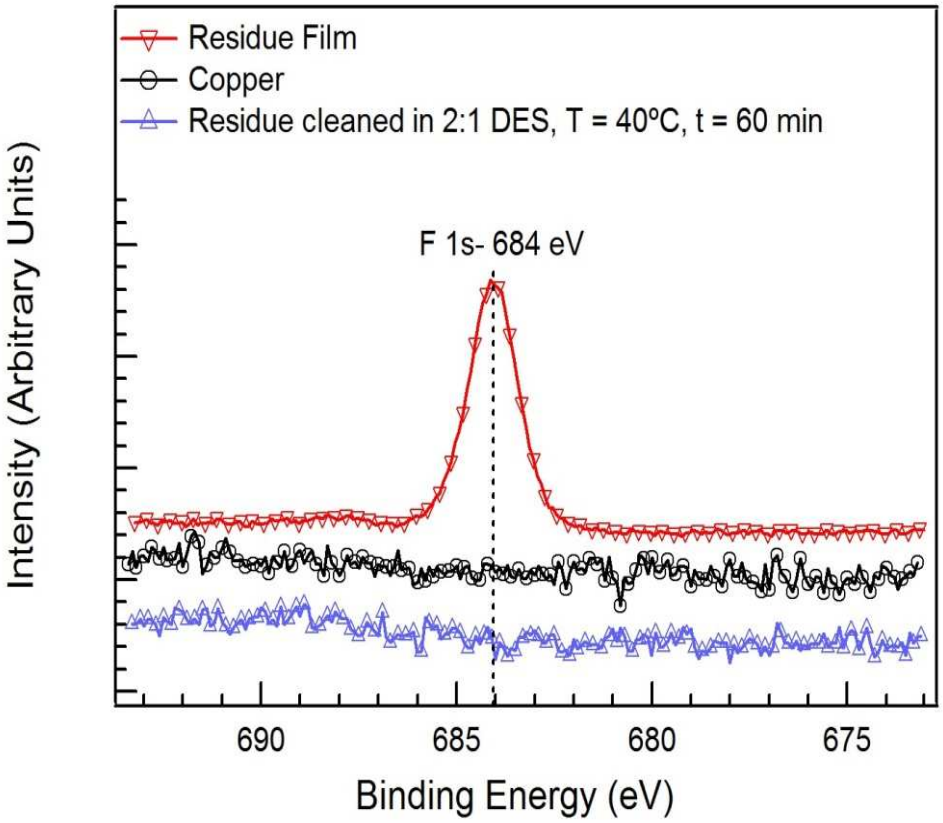
- Residue removal monitored using SEM imaging
- Complete removal of residue film observed within 60 minutes of cleaning

Confirmation of Residue Removal in 2:1 DES using XPS Analysis

Cu 2p spectrum



F 1s spectrum



- Residue removal exposes bare copper surface after cleaning

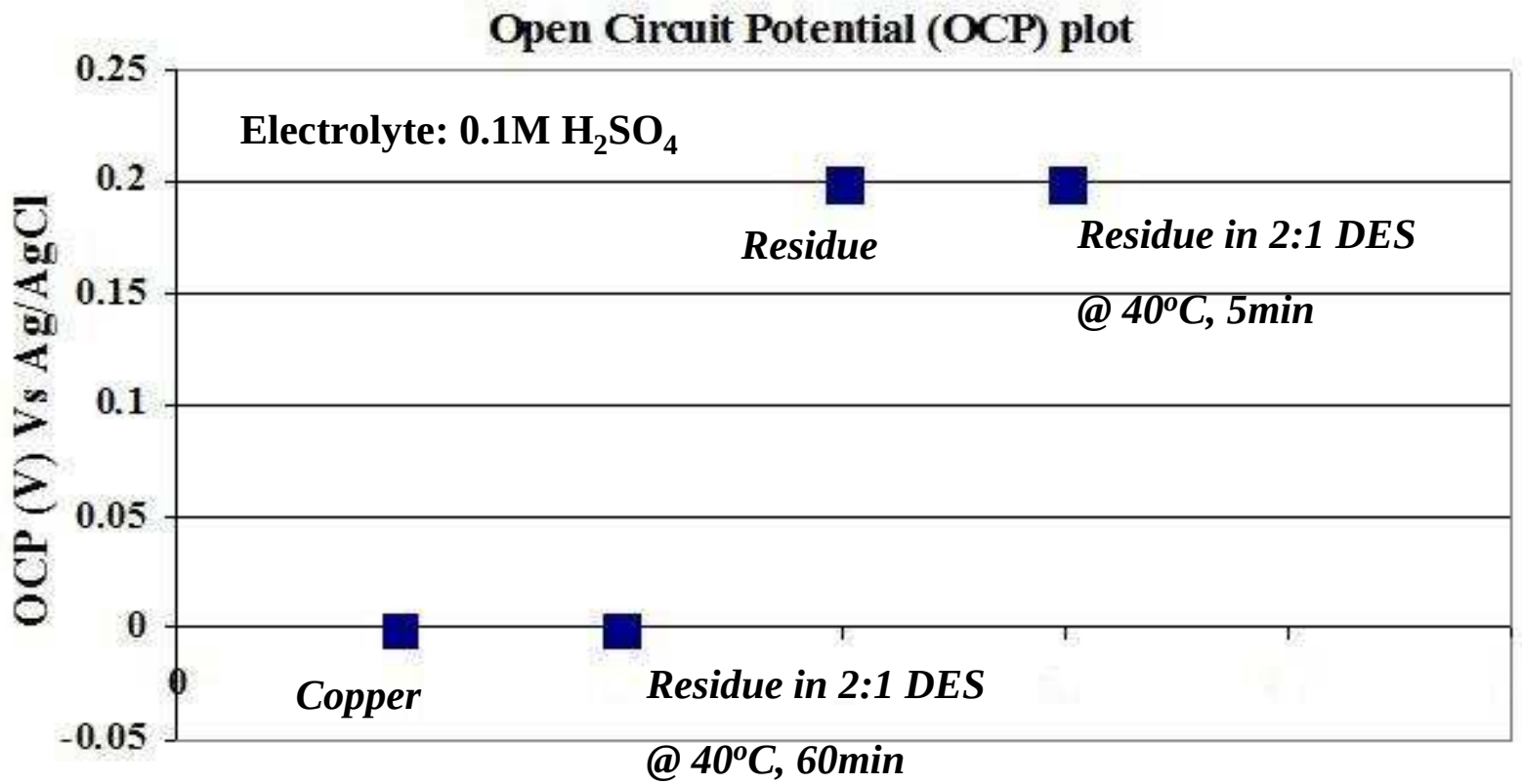
Cu 2p Spectrum

- Binding energies in sample cleaned in 2:1 DES at 40°C are identical to those for bare Cu

F 1s Spectrum

- Absence of fluorine peak in sample cleaned in 2:1 DES at 40°C –complete residue removal

Electrochemical Study to Confirm Residue Removal in DES



- Complete Removal

OCP of bare copper and sample cleaned in 2:1 DES at 40° for 60 min is same

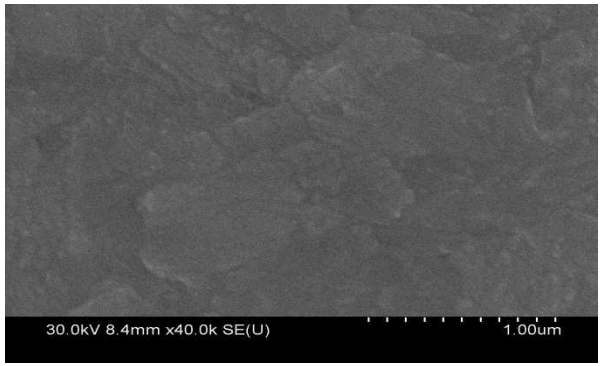
- Incomplete Removal

Higher OCP of residue film coated Cu exposed to 2:1 DES at 40° for 5 min indicates incomplete film removal

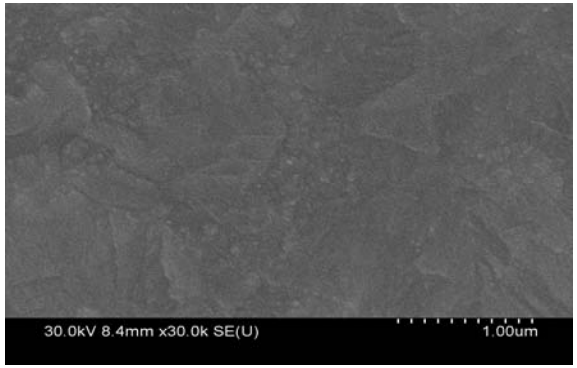
Comparison of Residue Removal in DES and Conventional Cleaning Formulations

- Cleaning Time: 30 min
- DES and conventional cleaning formulations are comparable—DES provides very low etch rate of dielectric

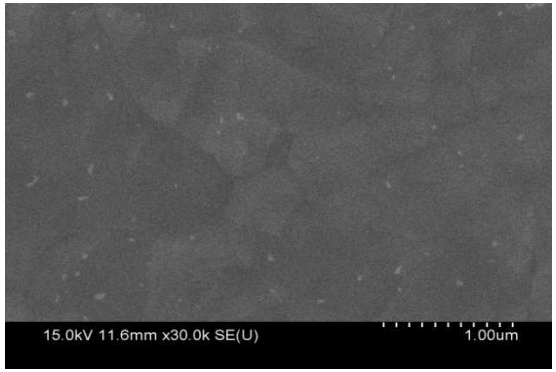
29% DMSO+1% NH_4F+70% H_2O

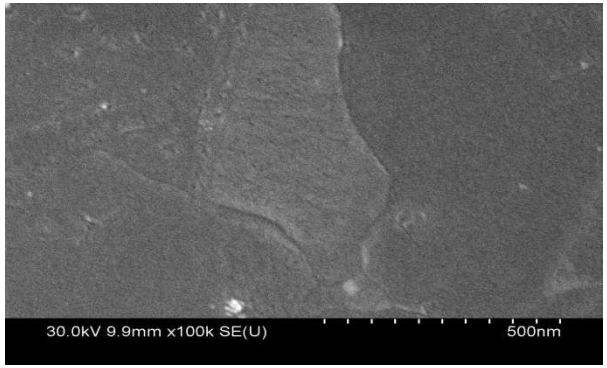


250:1 HF

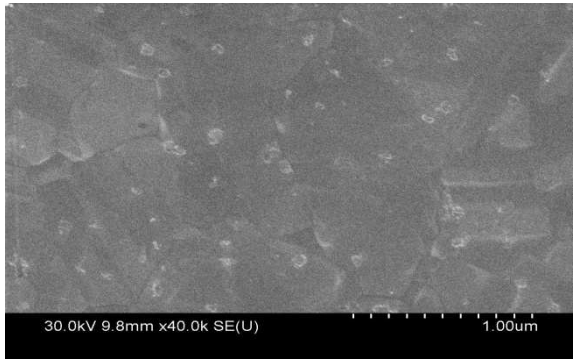


2:1 DES @ 40°C

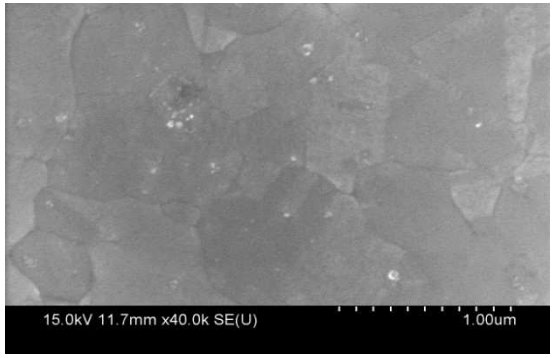




2:1 DES @ 70°C



3:1 DES @ 40°C



4:1 DES @ 70°C

Highlight of Results

- Deep eutectic solvent (DES) containing benign chemicals, choline chloride and urea, shows promise as a BEOL cleaning formulation
  - 2:1 DES at 40^{o}C and 70^{o}C effectively removed post etch residues on copper
  - Removal of post etch residues confirmed using X-ray Photoelectron Spectroscopy (XPS) and electrochemical techniques

Industrial Interactions

- Discussions with Dr. Robert Small, ***R.S. Associates, Tucson***
- Teleconference with Dr. Mansour Moinpour, Intel, to discuss results and seek advice on future direction

Acknowledgements

- Shariq Siddiqui, PhD, Materials Science and Engineering, University of Arizona
- Nandini Venkataraman, PhD, Materials Science and Engineering, University of Arizona

Future Plans

Next Year Plans

- Reduction of cleaning time, DES carry over, and operating temperature
- Rinsing of cleaned substrates—address any corrosion issues during rinsing
- Optimize formulation for the selective removal of post etch residue created from DUV resists
- Investigate cleaning of patterned test structures and determine the end point removal using electrochemical techniques

Long-term Plans

- Investigation of choline chloride/malonic acid as a cleaning formulation for post etch residue removal
  - Eutectic mixture of choline chloride with malonic acid possess a high solubility of copper oxides

Publications, Presentations, and Recognitions/Awards

Publication

- D. P. R. Thanu, N. Venkataraman, S. Raghavan and O. Mahdavi, " Dilute HF Solutions for Copper Cleaning During BEOL Processes: Effect of Aeration on Selectivity and Copper Corrosion", ECS Transactions, Volume 25, Issue 5, Page: 109-116 (2009)

Presentation

- D. P. R. Thanu, N. Venkataraman, S. Raghavan and O. Mahdavi, " Dilute HF Solutions for Copper Cleaning During BEOL Processes: Effect of Aeration on Selectivity and Copper Corrosion", 216th ECS Fall Meeting, Vienna, Austria, October 4-9 (2009)