Liquid Mixtures of Urea and Choline Chloride for Use in Back End of Line (BEOL) Cleaning

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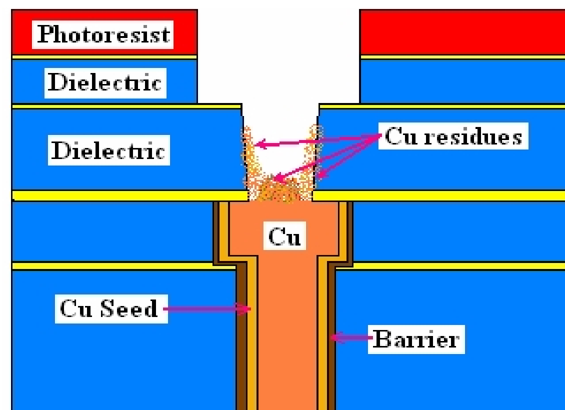
Objectives

OVERALL OBJECTIVE

- Develop cleaning formulations based on deep eutectic solvents (type of ionic liquids) to replace traditional organic solvent based formulations for BEOL cleaning of copper based structures

SPECIFIC OBJECTIVES

- Investigate the feasibility of using deep eutectic solvents (DES) based on choline chloride and urea for the removal of post etch residues
- Optimize cleaning conditions (DES composition and temperature) for complete removal of residues



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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%

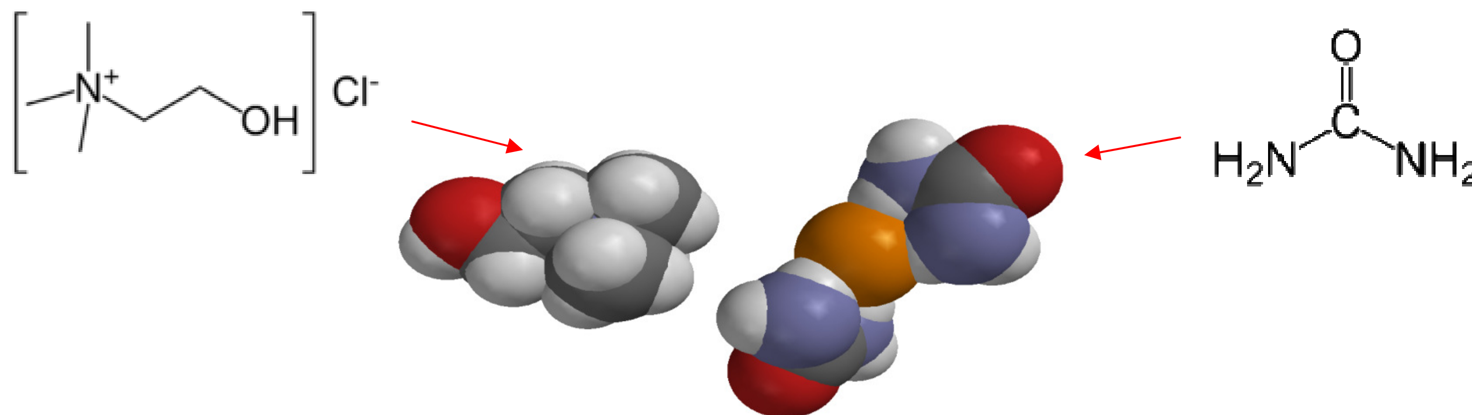
Ingredients	**LD_{50} (Oral Rat) mg/kg**
Urea	**8471**
Choline Chloride	**5000**

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

Deep Eutectic Solvents

- Low melting eutectic mixture of compounds- no traditional organic solvent in the composition
- ***Good conductivity***
- Viscosity can be lowered by mixing with suitable additives
- ***Low metal corrosion rate and high copper oxide solubility***
- ***Have wide electrochemical window (2-4 V)- much higher than organic solvents***

Eg: Eutectic mixture of choline chloride and urea



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Solubility of Metal Oxides in DES

Metal Oxides	Solubility in Choline Chloride/Urea (ppm)	Solubility in Choline Chloride/Malonic Acid (ppm)
Cu_2O	219	18337
CuO	4.8	14008
ZnO	1894	16217
FeO	0.3	5010
NiO	5	151

- Mechanism of metal oxide dissolution
  - Choline Chloride/ Urea- Forms complex of the form MClO $(Urea)^-$
  - Choline Chloride/Malonic Acid- Forms chlorometalate species of the form MCl_x^-

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

Deep Eutectic Solvents (DES)

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

T_f / °C

350
300
250
200
150
100
50
0

Liquid

Eutectic Point

70°C

40°C

12°C → Eutectic Temperature

Solid

2:1

3:1

4:1

0 20 40 60 80 100

100% Choline Chloride

Mole %

Eutectic Composition

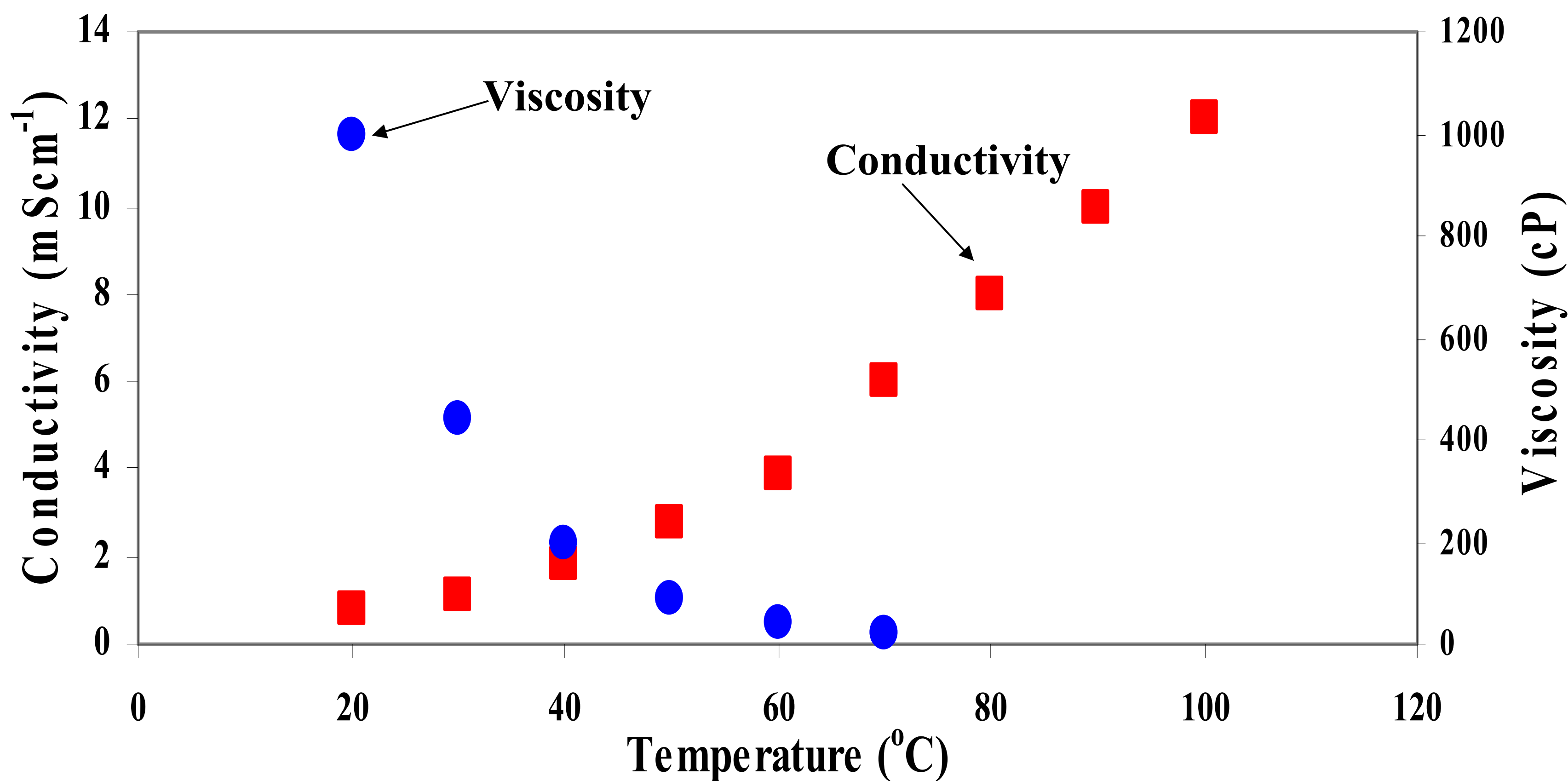
(Urea: Choline Chloride)

100% Urea

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

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

Conductivity, Viscosity and Surface Tension of Urea:Choline Chloride (2:1) DES at Different Temperatures



- Good conductivity (1 $mScm^{-1}$ @ 20°C)- comparable to 0.005 M KCl
- Conductivity increases and viscosity decreases with increase in temperature
- Surface tension: ~50 dynes/cm in the temperature range of 20 to 70°C

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Experimental Approach

Materials and Methods

- **Residue prepared from *g line* and *Deep UV (DUV)* photoresists**
- **Photoresists (*1.5 µm gline and 0.5 µm DUV)* spin coated on copper wafers and then ashed in Reactive Ion Etcher (RIE) using *CF_4/O_2 plasma; Ashing time: 8 min***
- **Thickness of residue film measured by Atomic Force Microscope step height measurements**
  - ***gline: ~30 nm (± 2 nm) and DUV: ~3 nm (± 1 nm)***
- **Residues characterized by X-ray Photoelectron Spectroscopy (XPS) analysis**

- **Residue removal investigated using *Scanning Electron Microscopy (SEM)* and confirmed using *XPS and electrochemical impedance spectroscopy* measurements**
- **Low-k dielectric etch rate measured using ellipsometry**

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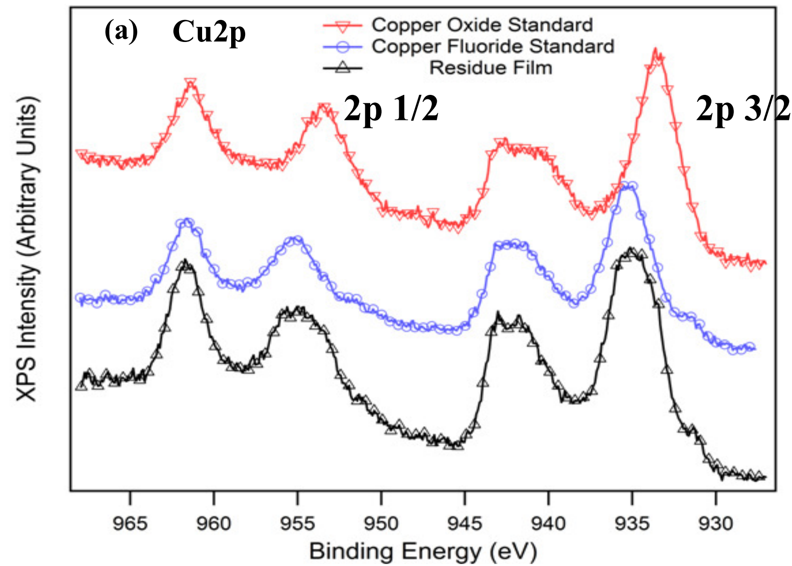
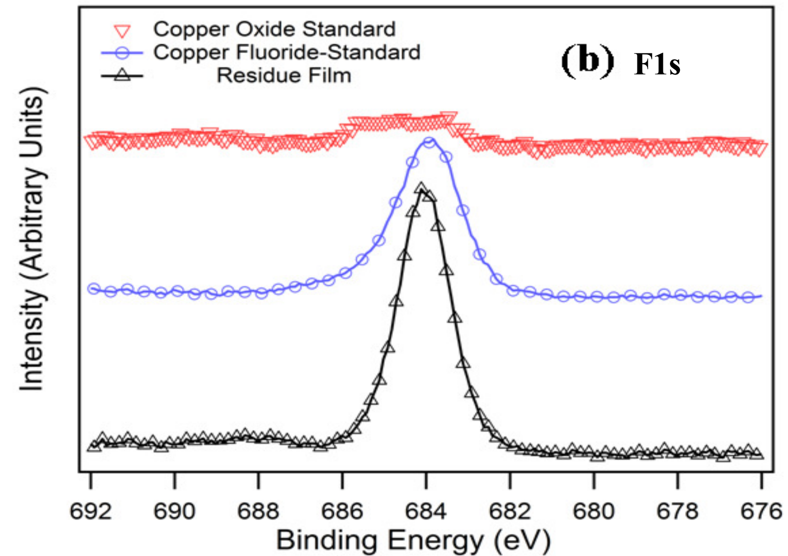
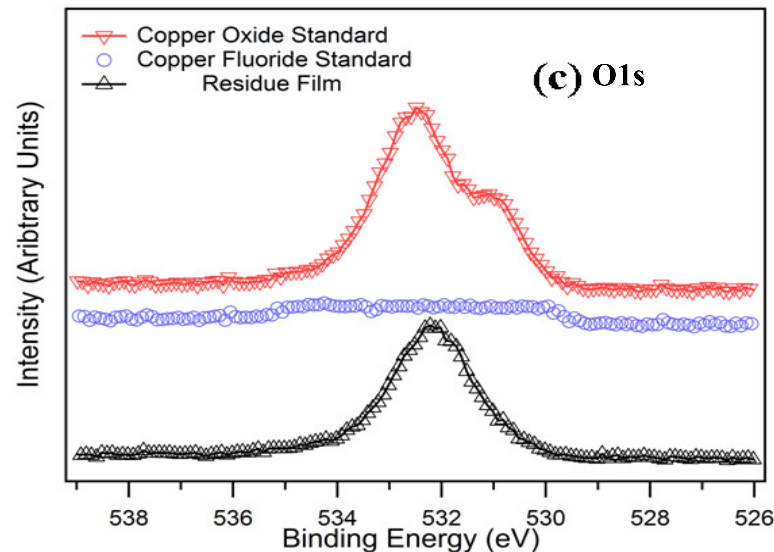
Oxidation State and Bonding of Elements in g-line Residue Film-Comparison with CuF_2 and CuO Standard



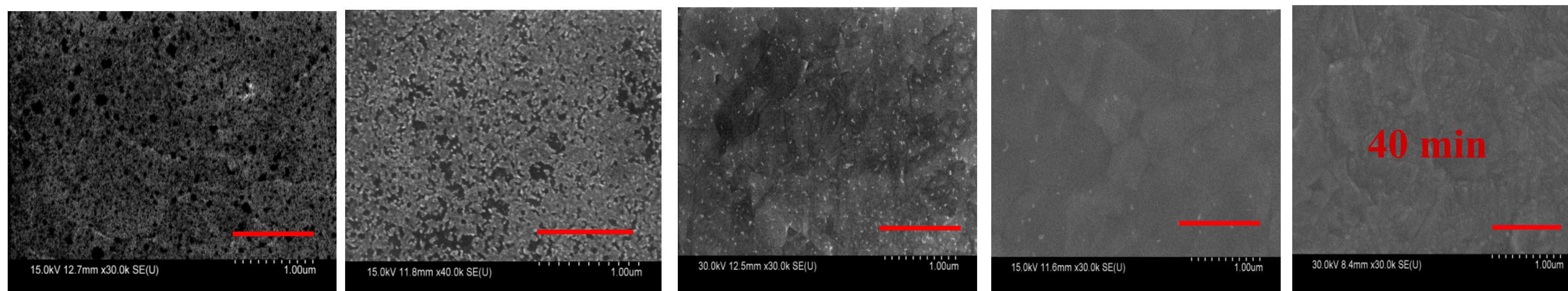




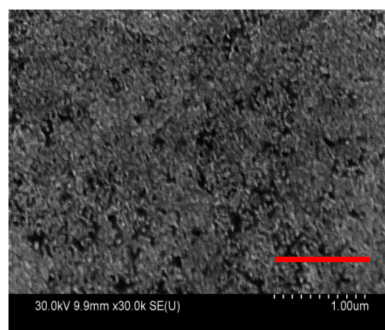
- g- line residue film contains mixture of CuO and CuF_2

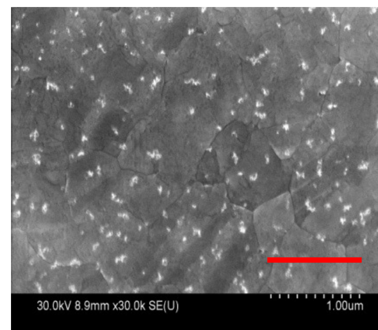
Residue Removal using 2:1 DES (Urea:Choline Chloride) at 40°C

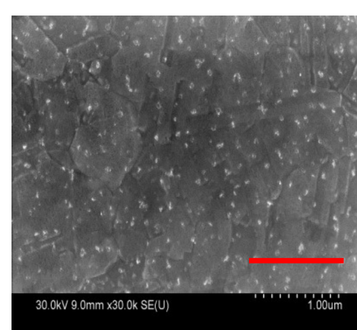
G LINE Residue (~30 nm)

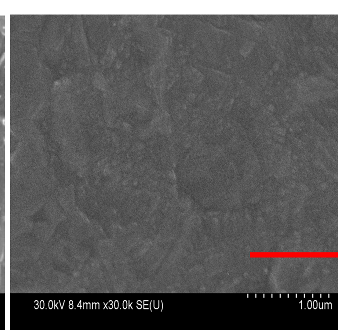


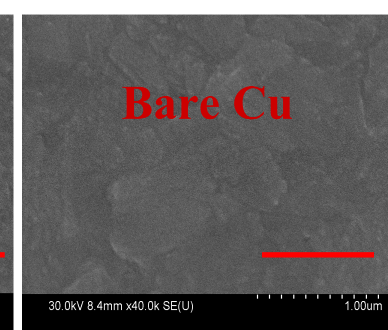
0 min | 5 min | 10 min | 30 min









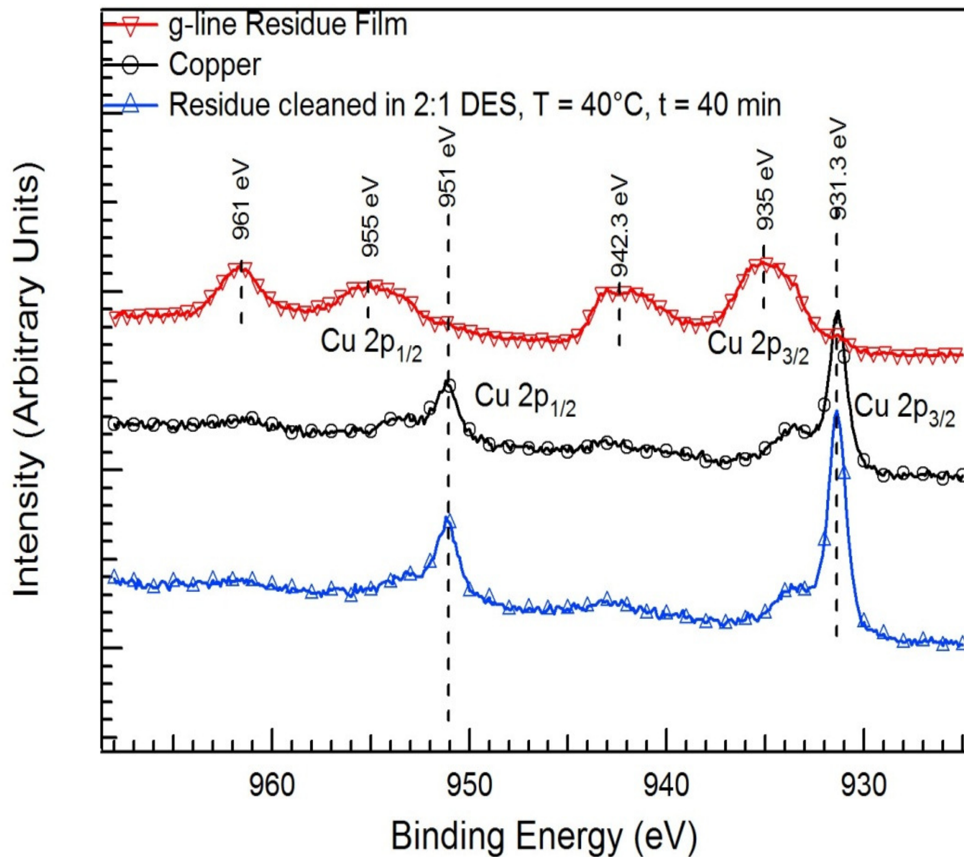


DUV Residue (~3 nm)

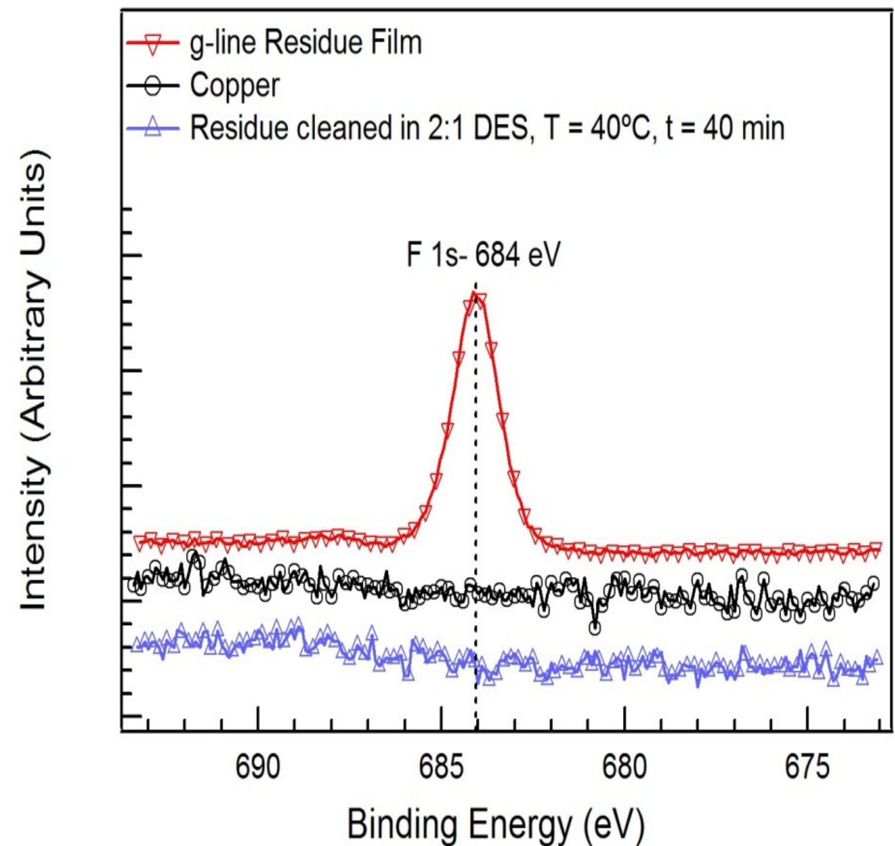
1 µm

- **Residue removed by immersion cleaning with stirring and monitored using SEM imaging**
- **Complete removal observed in *~30- 40 minutes* for gline residue and *~30 minutes* for DUV residue**
- **Removal rate of g line residue film is ~7.5 Å/min and DUV is ~1 Å/min using 2:1 DES @ 40°C**

Confirmation of g-line Residue Removal in 2:1 DES @40°C using XPS Analysis



Cu 2p spectrum



F 1s spectrum

- **Residue film shows the presence of Cu^{+2} compounds**
- **Cu 2p Spectrum: Cleaned samples shows absence of Cu^{+2} compounds**
- **F 1s Spectrum: *Absence of fluorine peak* in samples cleaned in DES- complete residue removal**

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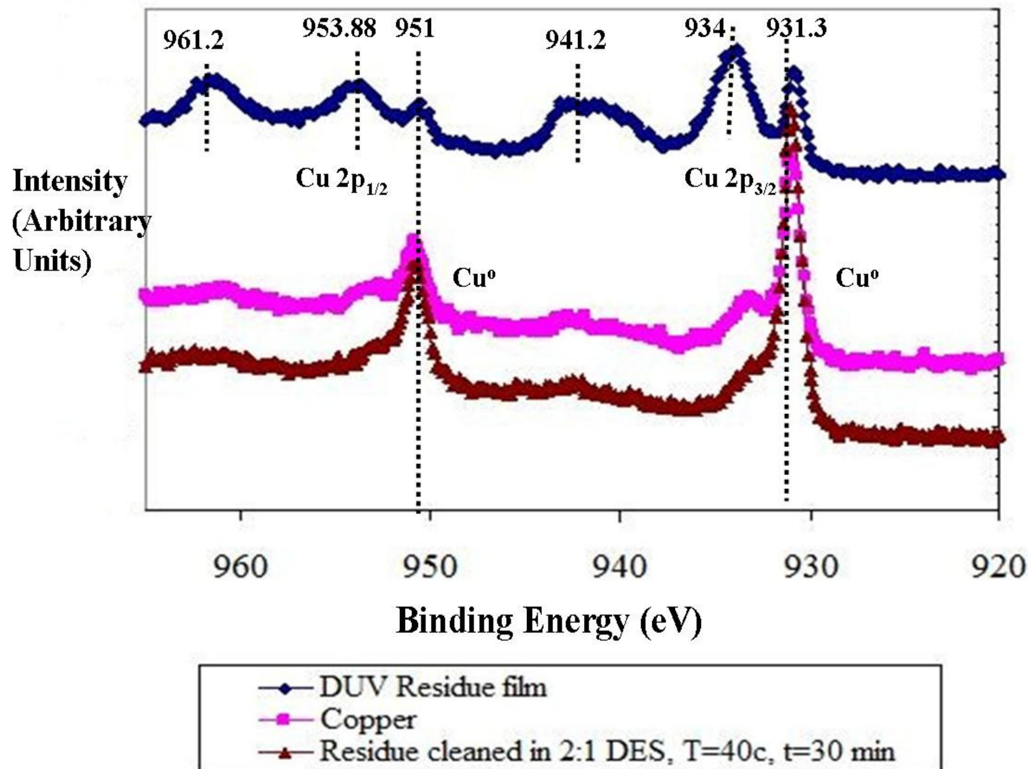
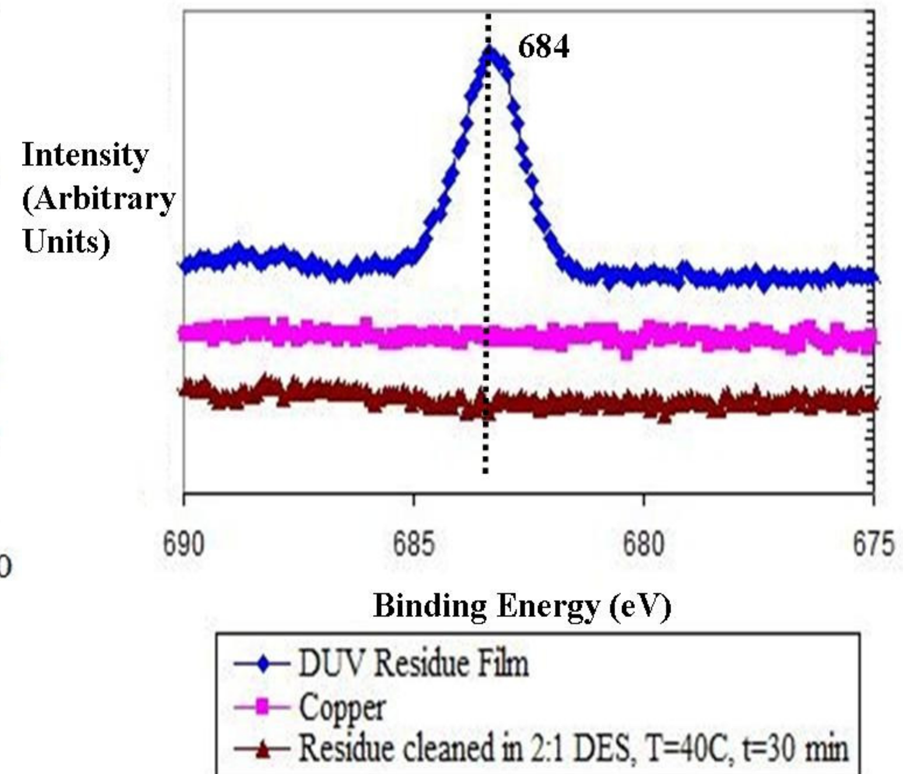
Confirmation of DUV Residue Removal in 2:1 DES @40°C using XPS Analysis



Cu 2p spectrum



F 1s spectrum

- Absence of Cu^{+2} compounds in Cu 2p spectrum and absence of fluorine peak in F 1s spectrum indicates complete removal of residue film

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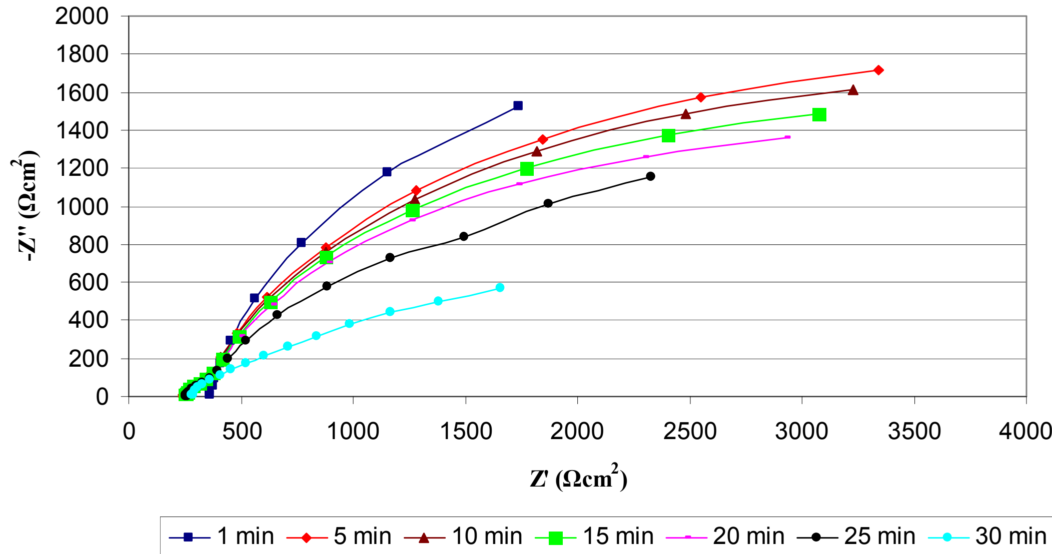
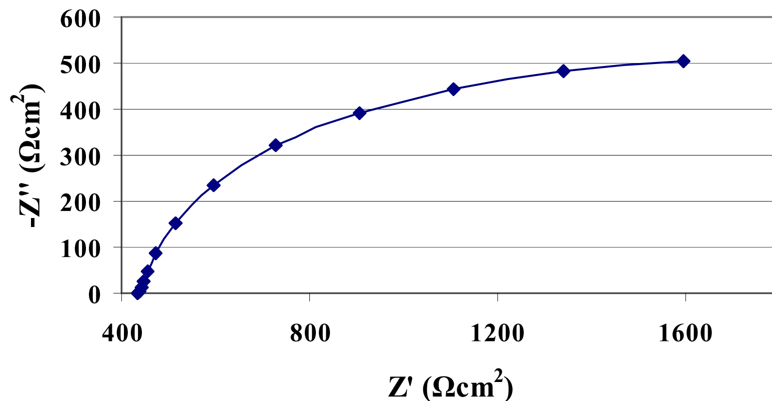
Electrochemical Impedance Spectroscopy Measurements

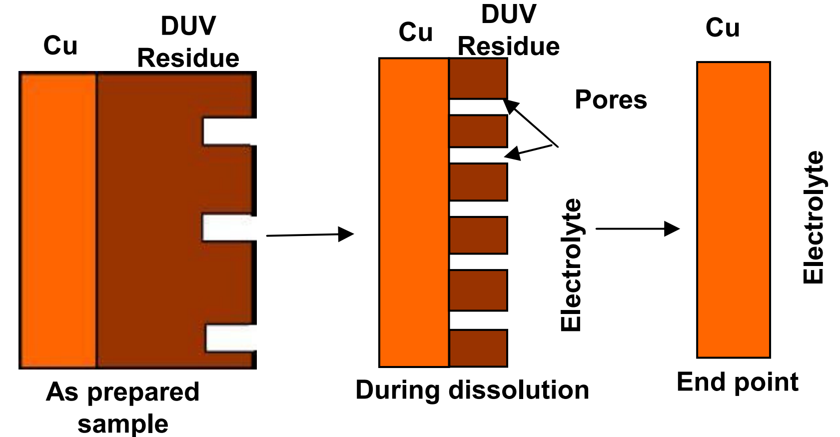


Impedance Spectra of DUV residue film as a function of time in 2:1 DES @40°C

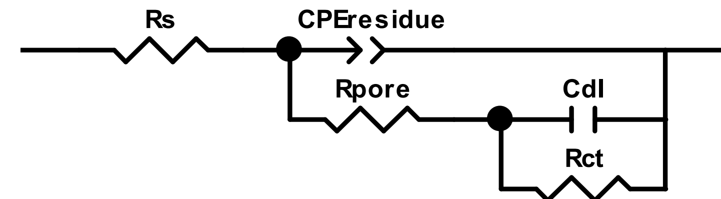


Impedance Spectrum of copper in 2:1 DES @40°C

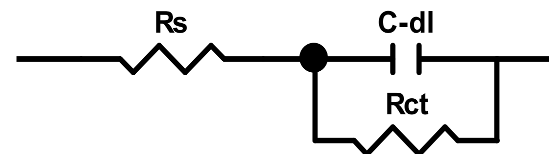
Porous Film Model



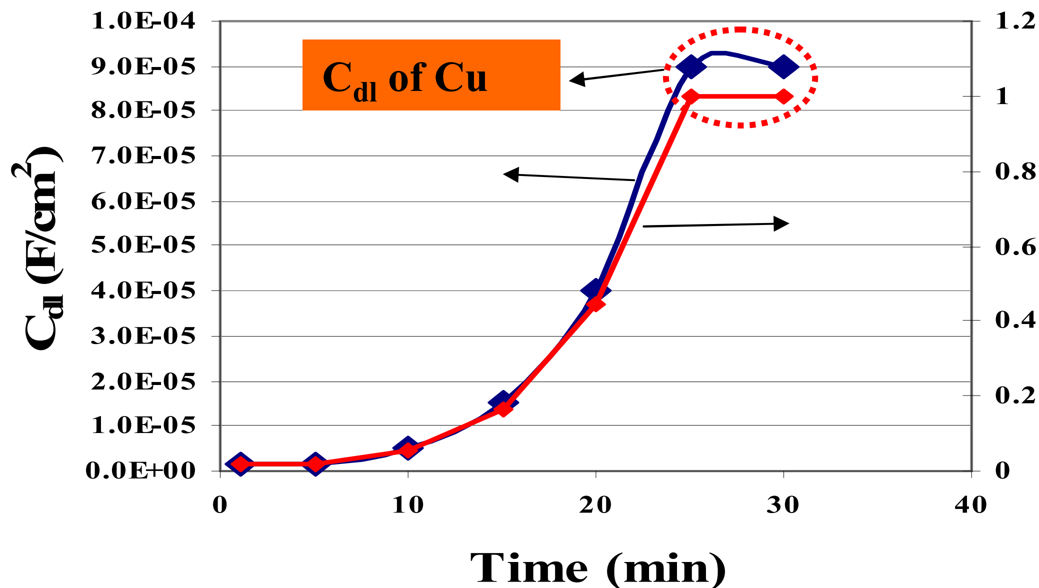
Equivalent circuit

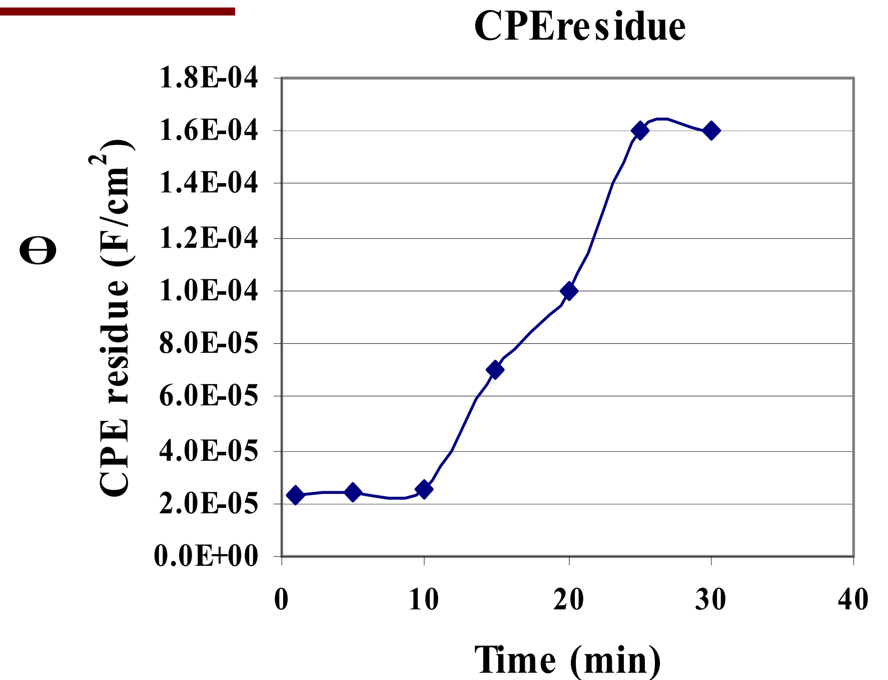


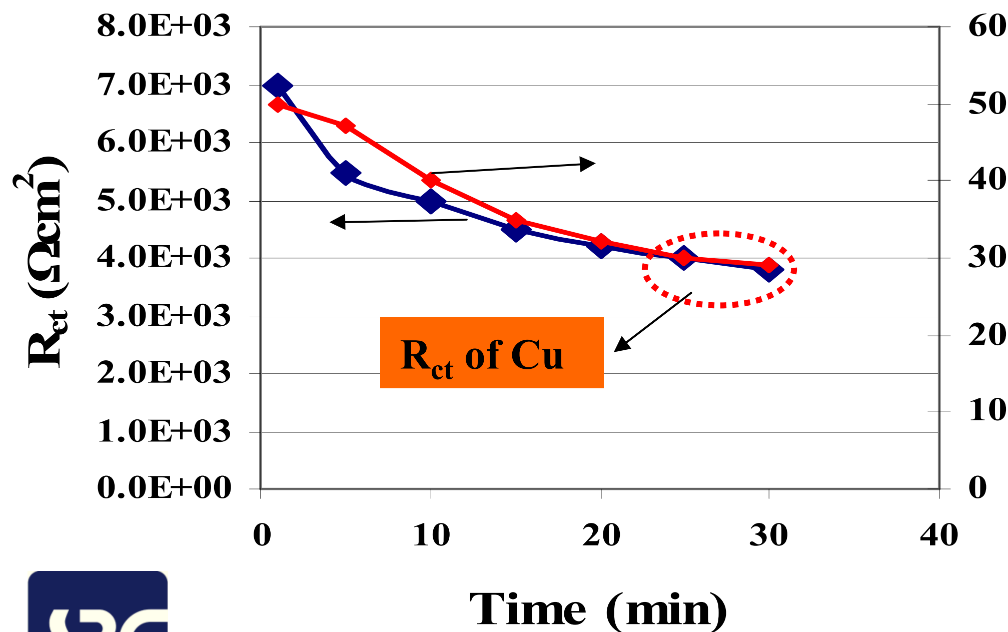
- Measured data at different times form a depressed semicircle
- Porous film model provides a good fit to the DUV residue film data



Porous Film Model







During dissolution

- C_{dl} ↑ and R_{ct} ↓ due to increased Cu surface area
- CPE $_{residue}$ ↑ and R $_{pore}$ ↓ due to loss of residue

At end point,

- C_{dl} of residue and R_{ct} values identical to that of bare Cu
- Area fraction of copper exposed reaches one where $\Theta = C_{dl}$ (residue)/ C_{dl} (Cu)

Etch Rate of Blanket *low-k Dielectric* in Different Cleaning Formulations

Etch Rate (Å/min)

0, 2, 4, 6, 8, 10, 12, 14, 16

29% DMSO+1% NH_4F+70% H_2O

250:1 HF

2:1 DES@ 25ºC

2:1 DES@ 40ºC

2:1 DES@ 70ºC

3:1 DES@40ºC

4:1 DES@70ºC

- DES provides *lower dielectric etch rate* compared to conventional cleaning formulations

Conclusions

- ***Choline chloride and urea based DES*** shows promise as a BEOL cleaning formulation
    - ***2:1 DES at 40°C and 70°C*** effectively removed post etch residues on copper
    - Removal of post etch residues confirmed using X-ray Photoelectron Spectroscopy (XPS) and electrochemical techniques
    - DES formulations etched low-k dielectric at a ***rate much smaller*** than conventional cleaning formulations

Work In Progress

- Study cleaning of just etched and under etched residue samples prepared from DUV photoresist
- Investigate stripping of photoresist and removal of post etch residues in ***patterned test structures*** using DES
- Reduction of DES viscosity by adding water and isopropyl alcohol
- Systematic analysis of another DES system as a cleaning formulation for post etch residue removal e.g. ***choline chloride/malonic acid***
    - Eutectic mixture of choline chloride with malonic acid has a high solubility for copper oxides

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

0 min

S-4800 15.0kV 5.9mm x100k SE(U) 1/12/2011 500nm

5 min

S-4800 15.0kV 5.8mm x100k SE(U) 1/12/2011 500nm

10 min

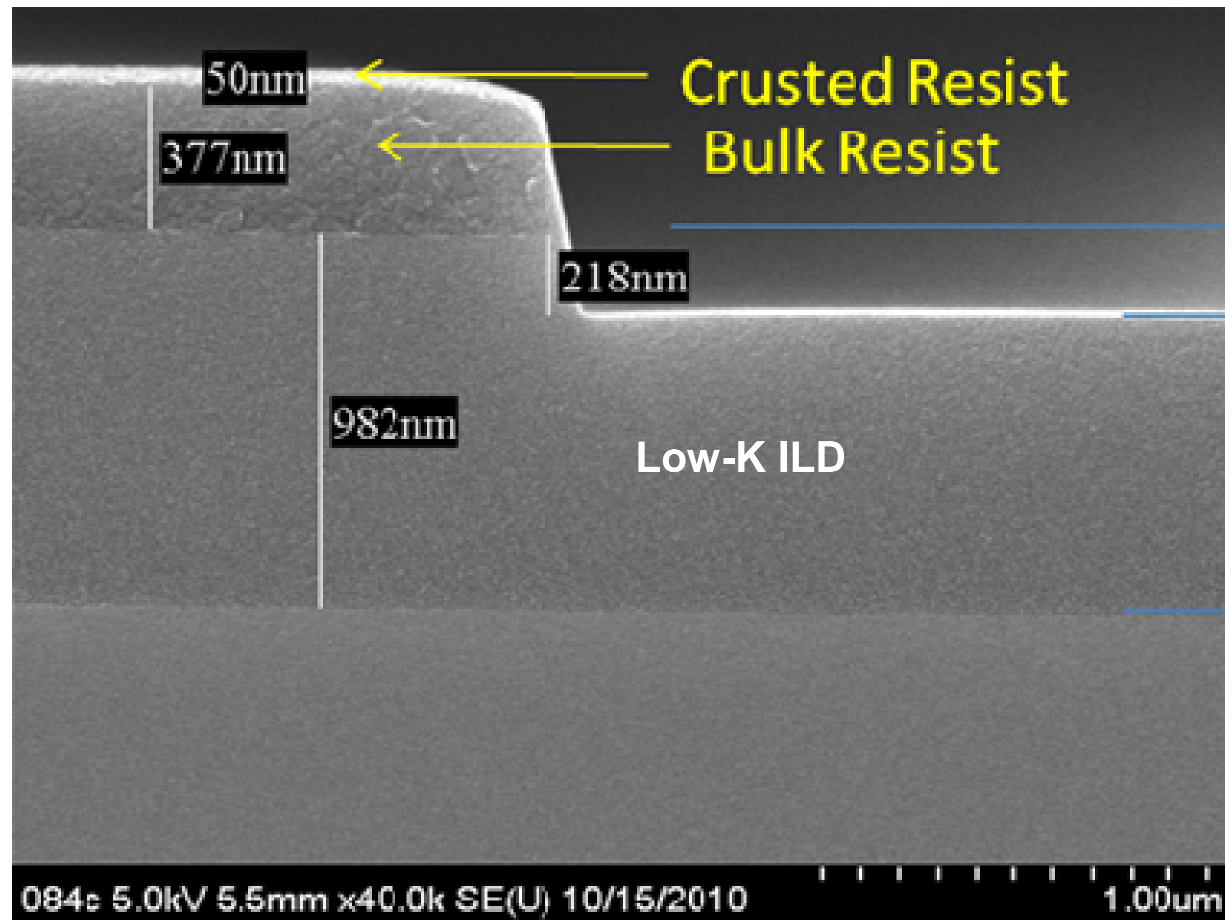
S-4800 15.0kV 5.5mm x100k SE(U) 1/12/2011 500nm

15 min

S-4800 15.0kV 5.5mm x100k SE(U) 1/12/2011 500nm

- **Residue removal observed within 15 minutes of cleaning**

Intel Patterned Wafers



- Crust and photoresist removal using DES is currently being investigated

Industrial Interactions and Technology Transfer

- Teleconference with Dr. Kanwal Singh and Bob Turkot, Intel, to discuss results and seek advice on future direction
- Presentation given by Dr.Raghavan at IMEC, Sep 2010, Leuven, Belgium
- Invention disclosure filed on September 28, 2010 at University of Arizona

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