Task ID: 425.034

<u>**Task Title</u>**: Improvement of ESH impact of Back End of Line (BEOL) cleaning formulations using ionic liquids to replace traditional solvents</u>

Deliverable: Report on the identification and procurement of ionic liquids

II. Technical Results:

Residue films were prepared by spin coating DNQ based photoresist films on copper and etching them in CF_4/O_2 plasma. A class of ionic liquids called *Deep Eutectic Solvent (DES)* was chosen for investigations. A mixture of solid choline chloride and urea at a molar ratio of 2:1 has a eutectic temperature of ~ 25^oC and forms a DES. The temperature at which a mixture of urea and choline chloride becomes a liquid depends on the molar ratio of ingredients. Liquid mixtures with urea to choline chloride molar ratios of 2:1, 3:1 and 4:1 were used at room temperature, 40^oC and 70^oC respectively to clean the residues. Following cleaning, the samples were rinsed with DI water. The removal of residue film was characterized using a Hitachi S 4800 Field Emission Scanning Electron Microscope (FE-SEM).

Figure 1 A, which is a high magnification SEM image of the residue film on copper, clearly shows the presence of a rough film with a number of pores. Cleaning in 2:1 DES at room temperature results in incomplete film removal, even after 60 minutes (Figure 1 B.) Mixtures with 3:1 and 4:1 molar ratio of urea to choline chloride appear to remove most of the residue at 40° C and 70° C in about ten minutes, as shown in Figure 1 C and 1 D. Complete removal of the residue film was achieved in these compositions in 30 minutes (Figure 1 E and 1 F).



Figure 1: High magnification SEM image of A) residue film prepared using CF_4/O_2 plasma on copper and residue film cleaned in B) 2:1 urea: choline chloride at room temperature for 60 minutes, C) 3:1 urea: choline chloride at 40°C for 10minutes, D) 4:1 urea: choline chloride at 70°C for 10minutes E) 3:1 urea: choline chloride at 40°C for 30minutes and F) 4:1 urea: choline chloride at 70°C for 30minutes

Summary:

Mixtures containing urea and choline chloride at a molar ratio of 3:1 and 4:1, wth a melting point of 40° C and 70° C respectively, can be used to effectively remove fluorinated etch residues on copper. These liquid mixtures are slight variations of the deep eutectic solvent (DES) made from 2:1 molar ratio of the same compounds.