# Ionic liquids – a new path to form nanothin seed films for CMOS applications

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The scaling of feature size in micro-electronics becomes difficult below 32 nm. At this stage, the copper seed layer occupies a considerable fraction of the feature size which makes the bottom-up filling difficult. Therefore, attempts are made to avoid the deposition of this copper seed and to electrodeposit directly on the barrier layer. However, the currently used Ta/TaN barrier layer forms an insulating oxide layer when it comes in contact with water, resulting in bad nucleation densities and poor adhesion of the deposited copper. Hence, people have started to look for alternatives such as replacing the Ta/TaN barrier material by ruthenium. The research reported here takes an alternative approach. Rather than changing the barrier material, the possibility of direct electrodeposition of copper on Ta is studied using electrolytes that do not contain water. More specifically, we have studied the direct electrodeposition of copper from ionic liquids on Ta/TaN barriers.

A variety of copper salts ($CuCl_x$, $Cu[Tf_2N]_x$, $Cu[BF_4]_x$ Cu-tartrate) and pyrrolidinium- and imidazolium-type ionic liquids (BMP[$Tf_2N$], EMIm[$Tf_2N$], EMIm[Cl], DMIm[$BF_4$]) were tested for the deposition of copper on blanket non-oxidized tantalum. The effect of different additives (saccharin, polyethylene glycol, benzotriazole, thiourea, 2-picolinic and glyoxilic acids etc.) was tested in ionic liquids. As shown by steady-state voltammetry, the surfactants in ionic liquids have complicated adsorption-desorption behavior, which can be due to the layering effect and the surface activity of the ionic liquids themselves. Clear hysteresis was observed at cathodic voltammograms acquired in pure ionic liquids. The structure and morphology of the copper films on Ta strongly depends on the type of ionic liquid and the additives. Nucleation densities greater than $10^{16}$ nuclei per $m^2$ were obtained from copper bistriflimide ionic liquids. According to TEM cross sections, closed, strongly adhering and uniform copper films with a thickness smaller than 10 nm can be deposited from ionic liquids directly onto Ta/TaN barriers. The influence of electrolyte composition on superfilling properties and the formation of oxide at Cu/Ta interface was also shown.