Quantitative chemical speciation of copper electro-deposition studied by STXM

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Electrodeposition of copper metal is used for interconnects in silicon integrated circuits. [1] while specific Cu(I) species are generated electrochemically in some solar cell devices [2]. These applications and others require copper at a desired oxidation state. However unlike noble metals such as Pt, copper is easily oxidized under various conditions [3]. Corrosion studies also require oxidation state speciation. Localized corrosion reactions are often involved. Spatially resolved techniques are needed to get detailed information about corrosion mechanisms, electrochemical stability and the influence of morphology on corrosion rates [4,5]. Electrochemical methods and spectromicroscopy techniques are actively employed in both metal electro-deposition and corrosion fields. We use soft X-ray scanning transmission X-ray microscopy (STXM) to study *ex-situ* and *in-situ* electrochemical processes with quantitative chemical speciation analysis at a spatial resolution of 30 nm [6,7]. In-situ electrochemical measurements in STXM have been demonstrated [8] and are the target of the present studies of copper electrodeposition.

The formation of different copper species is strongly influenced by both pH and potential [9,10]. We have used STXM to study copper electrodeposition from Cu sulfate solutions at different pH and at a range of potentials, under conditions where different copper species can be formed electrochemically in a controlled manner [9,10]. We have used spectromicroscopy at the Cu 2p and O 1s edges to speciate and quantitatively map different copper species. *Ex-situ* samples were prepared using a gold seeding electrode as working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode in a 3-electrode configuration. *In-situ* experiments use a gold working electrode and a Cu pre-coated gold electrode as counter electrode in a 2-electrode configuration. *In-situ* studies provide detailed kinetic and mechanistic information. [11]

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