Focused E-Beam-Driven Liquid-Phase Surface Modification of Metals

Electron beam-mediated processes are an effective means of achieving localized material modification through both etching and deposition. We present a technique to directly modify metallic surfaces through etching and deposition using liquid-phase, focused electron-beam-mediated processes. In our approach, we employ an electrohydrodynamically delivered water-ammonia thin liquid precursor film on a copper surface. Upon electron-beam irradiation, radiolytically generated redox species induce two distinct chemical and morphological regimes. Under net oxidizing conditions, which arise when the film has a lower ammonia concentration, copper is etched from the surface. Conversely, a higher ammonia concentration shifts the balance toward a reduction-dominant regime, suppressing concentration of radiolytic oxidizing species and prompting the release of Cu ions or ion complexes into the film secondary to non-radiolytic surface oxidation, ultimately leading to the redeposition of copper. We use experiments and simulations to highlight the interplay among ammonia concentration, electron-beam-induced radiolysis, and diffusional transport. This work extends the capabilities of e-beam-assisted surface processing in liquid environments, suggesting new pathways for nanoscale, site-specific metal modification.