Etching of copper using liquid reactants and a focused electron beam

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Liquid phase electron-beam-induced-processing (LP-EBIP) is a maskless and direct-write process where an electron beam induces chemical reactions in bulk liquids. Previous efforts in LP-EBIP have focused primarily on the deposition of metal nanostructures, with the exception of etching silicon nitride in a KOH solution.[*] Here we demonstrate the electron beam mediated etching of a copper surface using liquid reactants, the latter which are maintained in an environmental SEM. This approach potentially allows for etch selectivity to underlying dielectrics, a limitation for FIB based etching methods.

Etching was performed with a FEI Quanta FEG operating in ESEM mode using an accelerating voltage and beam current of 30 kV and 550 pA, respectively. Solutions containing various mixtures of ferrous sulfate, sulfuric acid and sodium dodecyl sulfate were used for the etching process (illustrated in figure 1(a)). The liquid reactant was maintained by a combination of substrate cooling (Peltier stage) and saturated water vapor conditions within the ESEM chamber.

An *in-situ* image of the etching process is shown in figure 1(b), where the indicated dark regions represent primary beam impact areas. SEM images of the final etch product are shown in figure 2. Figures 2(a) and 2(b) are from a solution of $FeSO_4$, H_2SO_4 and SDS, while figures 2(c) and 2(d) are from a solution of H_2SO_4 and SDS. Iron ions, although a main component in copper wet-etching, appear to suppress the etch rate when compared to solutions without iron. This is apparent when comparing the tilt figures 2(b) and 2(d), the latter which shows that the electron beam has clearly facilitated localized etching. The etch process in figure 2(d) penetrates through the ~100 nm Cu layer to reveal the underlying Si substrate. This is confirmed by EDX analysis of the etch pit center vs. the surrounding Cu layer reference. Finally, the etched regions shown in figures 2(a) and 2(c) are all performed with the same area scan and dose ($0.67\ C\ cm^{-2}$), but reveal varying etch rates. This is likely due to the increasing thickness of the liquid droplet as etching is performed further from the liquid-substrate interface.

The chemical mechanism for this process is currently under investigation and will be discussed further, along with the prospect for resolution improvements and extendability to other material sets.

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[*] Donev EU, Samantaray C, Bresin M, and Hastings JT**.** Recent Advances in Liquid Phase Electron Beam Induced Processing: Silicon Nitride Etching and Palladium Deposition. *MNE London* 2013.

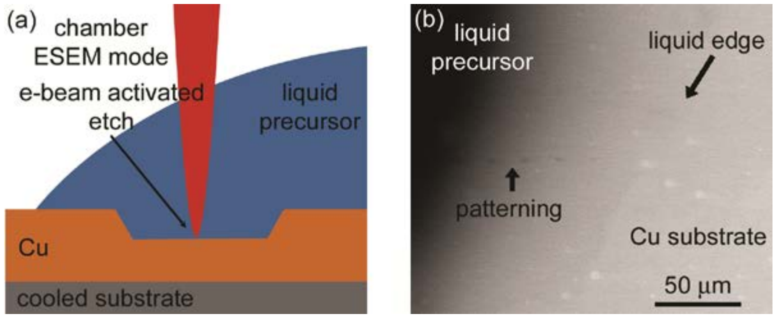

Figure 1: (a) Schematic illustration of LP-EBIP etching process. (b) *In-situ* ESEM image of the droplet along with indications of patterning.

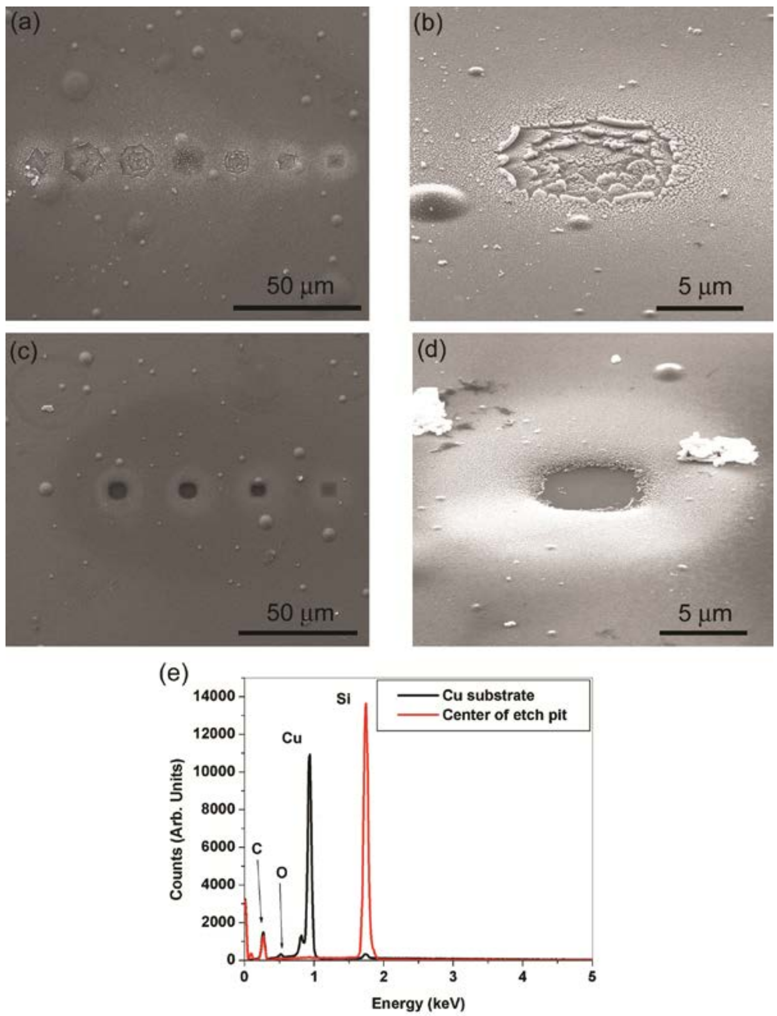

Figure 2: SEM images of the etching process and EDX results. (a) Example etching with $FeSO_4$, H_2SO_4 and SDS, where the rightmost etched region lies closest to the liquid-substrate interface and (b) 60° tilt image of an etched region. (c) Etching with a solution of H_2SO_4 and SDS showing increased etch rates. (d) 60° tilt image of H_2SO_4 and SDS demonstrating etching to the underlying Si substrate. (e) EDX spectra of the reference Cu substrate (black line) and the center of an etch pit (red line), the latter similar to the center shown in panel (d).