

Liquid-phase electron-beam-induced-deposition on bulk substrates without liquid cells

M. Bresin, N. Nehru, and J. T. Hastings
*Department of Electrical and Computer Engineering,
University of Kentucky, Lexington, KY 40517
todd.hastings@uky.edu*

Liquid phase electron-beam-induced-deposition (LP-EBID) is a maskless and direct-write process where an electron beam induces chemical reactions in bulk liquids. Previous work in LP-EBID has shown the successful deposition of a variety of metals from aqueous precursors, resulting in high purity gold, silver, and platinum deposits.* However, deposition in LP-EBID has previously relied on commercial liquid cells, wherein the precursors are isolated from the vacuum chamber. While cell-based precursor isolation is useful for applications such as liquid phase imaging, it presents practical limitations on substrate choice for direct-write deposition. In this work, the authors demonstrate cell-less LP-EBID on bulk Si substrates with an environmental scanning electron microscope (ESEM). The ESEM enables the hydration of precursor crystals, forming an in-situ liquid precursor that can be used for patterning. The ability to deposit on bulk substrates overcomes a major technical hurdle for LP-EBID, potentially allowing for process scaling. The process, along with strategies for deposition improvement, will be discussed.

The precursor AgNO_3 was used for this demonstration of cell-less LP-EBID. Deposition was performed with a FEI Quanta FEG operating in ESEM mode with a 20 keV beam energy and 150 pA beam current. The deposition process is illustrated in figure 1, where solid precursor is hydrated by decreasing the substrate temperature to 4° C, followed by an increase in the chamber H_2O pressure to approximately 6 torr. Liquid edges can be advanced or receded by fine control of the chamber pressure. Once the precursor crystals are sufficiently hydrated, the electron beam is scanned on the liquid edge to deposit the desired material on the substrate. SEM images for this process are shown in figure 2. Figs. 2(a) and 2(b) show the AgNO_3 salt crystals pre- and post-hydration respectively. In-situ patterning is shown in fig. 2(c), where the pattern is confined to the liquid while not extending to the substrate. Patterns remain visible upon liquid removal (fig. 2(d)), likely where the liquid edge was sufficiently thin for beam penetration to the substrate. A comparison of EDX data for AgNO_3 salt crystals vs. deposited structures is shown in fig. 2(e). The salt crystal contains a strong nitrogen peak as expected, which is not observed in the deposition spectra. Quantification of the deposits indicates highly pure Ag, with C and O components consistent with the substrate reference.

* G. Schardein et al., *Nanotechnology*, vol. 22, p. 015301, 2011; E. U. Donev and J. T. Hastings, *Nano Letters*, vol. 9, pp. 2715-2718, 2009; L. E. Ocola et al., *J. Vac. Sci. Technol. B*, vol. 30, 06FF08-7, 2012.

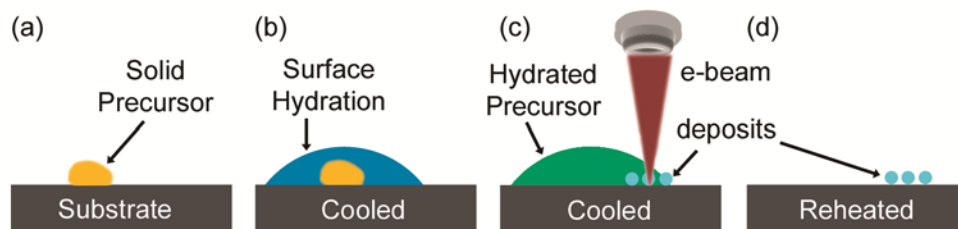


Figure 1: Schematic illustration of LP-EBID on bulk substrate without liquid cells. (a) Solid precursor placed on substrate. (b) Substrate temperature cooled to 4° C and chamber H₂O vapor pressure increased to ~6 torr, causing surface condensation. (c) Hydrated precursor patterned with electron beam on thin edge. (d) Substrate returned to room temperature, removing the hydrated precursor while leaving irradiated deposits.

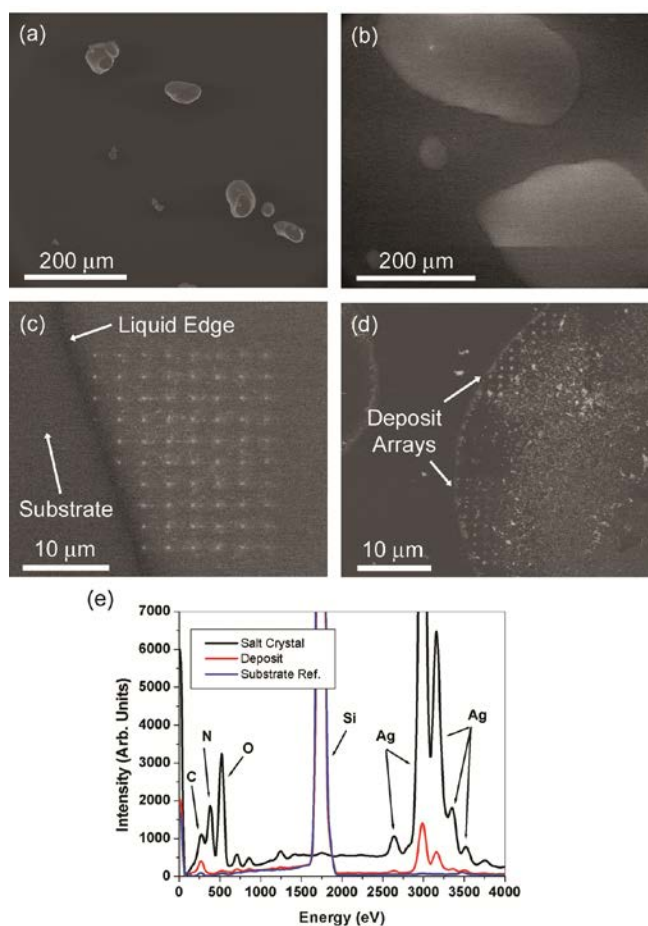


Figure 2: SEM images of the deposition process and EDX results. (a) AgNO₃ crystals pre-hydration. (b) Hydration of crystals. (c) In-situ patterning, where deposition dots are visible along the liquid edge and do not extend to the uncovered substrate. (d) Ex-situ image after liquid removal, showing the deposition region with defined pattern edges. (e) EDX spectra of AgNO₃ salt crystals (black), LP-EBID deposits (red), and substrate (blue). Similar compositions are found for C and O between the deposits and substrate spectra.