In-situ Microfluidics using a Liquid Injector for the Study of Beam Induced and Dynamic Processes

A. Botman, S. J. Randolph
FEI Company, 5350 NE Dawson Creek Drive, Hillsboro 97124 Oregon, US
aurelien.botman@fei.com

Beam chemistry within scanning electron microscopes (SEMs), where the electron beam decomposes a gaseous precursor to form a either a non-volatile deposit and a volatile residual fragment, or chemically enhances an etching reaction, is a well-established research field [1,2,3]. Promising new chemistries are currently being developed [4], but the playing field for chemistry selection is limited to precursors which exhibit adequate vapor pressures at chamber vacuum operating conditions.

In this paper we open up a new range of possibilities by demonstrating novel manipulation of liquids in vacuum. Previously, liquid precursors have been limited to either reliance on adequate vapor pressure for gas phase delivery, pre-spun films across entire wafers [5], or enclosed, membrane-covered cells, where the beam interaction takes place at the liquid-membrane interface [6]. Our system does not suffer from some of the disadvantages to these approaches, as we are able to work without pressure-separating membranes, and we may freely position the fluid locally at any time during the experiment.

Using our Liquid Injector System (LIS), consisting of coated borosilicate nanocapillaries, we are able to selectively deliver fluids and maintain liquid drops in systems operating in either environmental SEM mode (pressures between 0.1 and 10 mbar) [7] or high vacuum mode (lower than 1×10^{-4} mbar). The LIS tip can be positioned inside a vacuum chamber at the sample working area and provides good flow control. Droplet size can be controlled reproducibly by varying the LIS tip diameter, chamber pressure and/or substrate temperature. This arrangement allows research into novel liquid nanochemistry applications, and observation of dynamic processes *in situ*, such as real-time electrodeposition and corrosion studies. Various fluids including salt solutions have been successfully tested. In this contribution we demonstrate our current *in situ* fluid manipulation capabilities.

We also demonstrate localized electrochemical deposition as an application of the novel technique. The electrolyte (aqueous $CuSO_4$) is injected at the desired position using the LIS, which also serves as the anode. The electron beam is used as a virtual cathode, allowing an electrochemical reaction to be performed at an arbitrary location on an insulating substrate. The advantages of electrochemical deposition are the extremely high material purity obtainable for a great abundance of precursors.

[1] A. Botman, J. J. L. Mulders, and C. W. Hagen, "*Creating pure nanostructures from electron-beam-induced deposition using purification techniques: a technology perspective*" Nanotechnology, 20, 372001, 2009.
[2] S. J. Randolph, J. D. Fowlkes, and P. D. Rack, "*Focused, Nanoscale Electron-Beam-Induced Deposition and Etching,*" Critical Reviews in Solid State and Material Sciences, vol. 31, no. 3, pp. 55-89, Sep. 2006.
[3] Utke, P. Hoffmann, and J. Melngailis, "*Gas-assisted focused electron beam and ion beam processing and fabrication,*" J. Vac. Sci. Technol. B, vol. 26, no. 4, p. 1197, 2008.
[4] A. Botman et al., "*Electron postgrowth irradiation of platinum-containing nanostructures grown by electron-beam-induced deposition from Pt(PF3)4,*" Journal of Vacuum Science & Technology B, vol. 27, no. 6, p. 2759, 2009.
[5] T. J. Stark, T. M. Mayer, D. P. Griffis, and P. E. Russell, "*Formation of complex features using electron-beam direct-write decomposition of palladium acetate,*" J. Vac. Sci. Technol. B, vol. 10, p. 2685, 1992.
[6] E. U. Donev and J. T. Hastings, "*Electron-beam-induced deposition of platinum from a liquid precursor,*" Nano Letters, vol. 9, p. 2715, 2009.
[7] M. Donald, "*The use of environmental scanning electron microscopy for imaging wet and insulating materials,*" Nature Materials, vol. 2, p. 511, 2003.

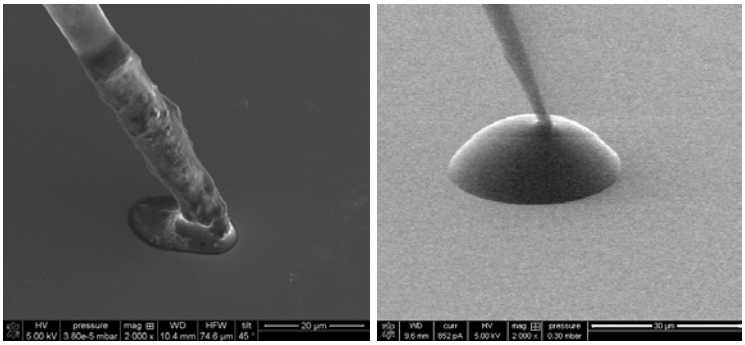

Figure 1: Tip of LIS touching down on sample (inclined at 45 degree tilt for better viewing), demonstrating delivery of pure water. The delivered, stable drop can be small (10-20 μm diameter, left) or significantly larger (right).

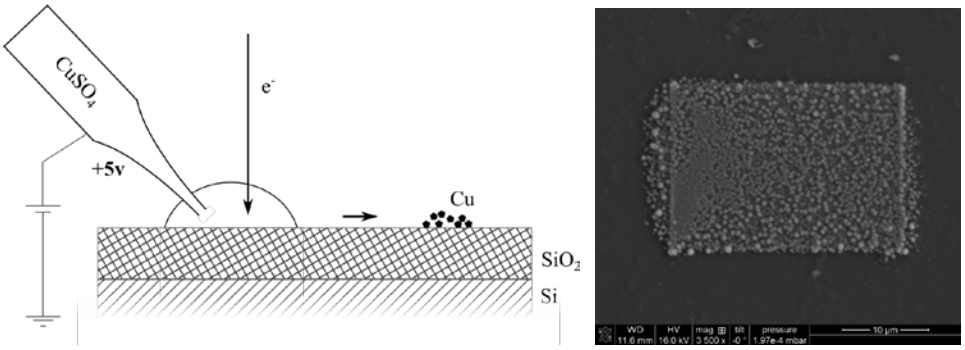

Figure 2: (a) Schematic illustrating principle of using the electron beam as a virtual cathode to electrochemically reduce delivered $CuSO_4$(aq) to Cu(s). (b) A square of pure Cu metal after reduction from CuSO4 by the electron beam. The beam was scanned in a square pattern which directly yielded the shape of the resulting deposit.