Laser Assisted Electron Beam Induced Deposition: Towards a Nanoscale Atomic Layer Deposition Process

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Electron beam induced deposition (EBID) is a direct-write process which can be used to selectively deposit material with nanoscale resolution. EBID utilizes a scanning focused electron beam to dissociate adsorbed precursor molecules which subsequently condense onto the substrate. One of the major limitations of the EBID process is low material purity resulting from incomplete by-product removal of the typically organometallic precursor. Therefore, the development of EBID purification strategies for enhanced materials functionality is a grand challenge for wider application of this synthesis technique.

While recently EBID deposits have been used as selective atomic layer deposition (ALD) catalyst[1], here we demonstrate an in-situ ALD-like process driven by electron and laser-induced thermal half reactions. We have developed an O_2-assisted laser anneal process to enhance the purity of patterns deposited using $MeCpPt^{IV}Me_3$ precursor gas as shown in the schematic in Figure 1[2]. Additionally we have demonstrated a laser assisted electron-beam-induced-deposition (LAEBID) process as an effective method to provide *in-situ* purification during deposition. The synchronized process is initiated by an approximately monolayer EBID cycle followed by a laser pulse which thermally desorbs by-products of the condensed phase. The process is repeated until the desired shape and size is achieved. The addition of a reactive gas and a synchronized electron and laser pulse begins to look a lot like a nanoscale atomic layer deposition process (ALD), however the half reactions are electron and thermally stimulated, respectively.

To circumvent some apparent issues with the LAEBID process, such as competition between reactive and precursor gases for absorption sites, we have developed an ALD-like process in which the gases are pulsed. In this process, precursor gas is first injected into chamber and EBID is used as a first half reaction to deposit a pattern with a controllable number of monolayer. A laser induced reactive gas "anneal" ensues as a second half reaction to purify the deposit. This process is repeated in a cyclic manner until a deposit of desired shape and thickness is obtained.

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[1] A.J.M. Mackus, S.A.F. Dielissen, J.J.L. Mulders, and W.M.M. Kessels, Nanoscale, 2012, **4** (15), 4477-4480.

[2] M.G. Stanford, B.B. Lewis, J.H. Noh, J.D. Fowlkes, N.A. Roberts, H. Plank, and P.D. Rack, ACS Appl. Mater. Interfaces, 2014, **6** (23), 21256-21263.

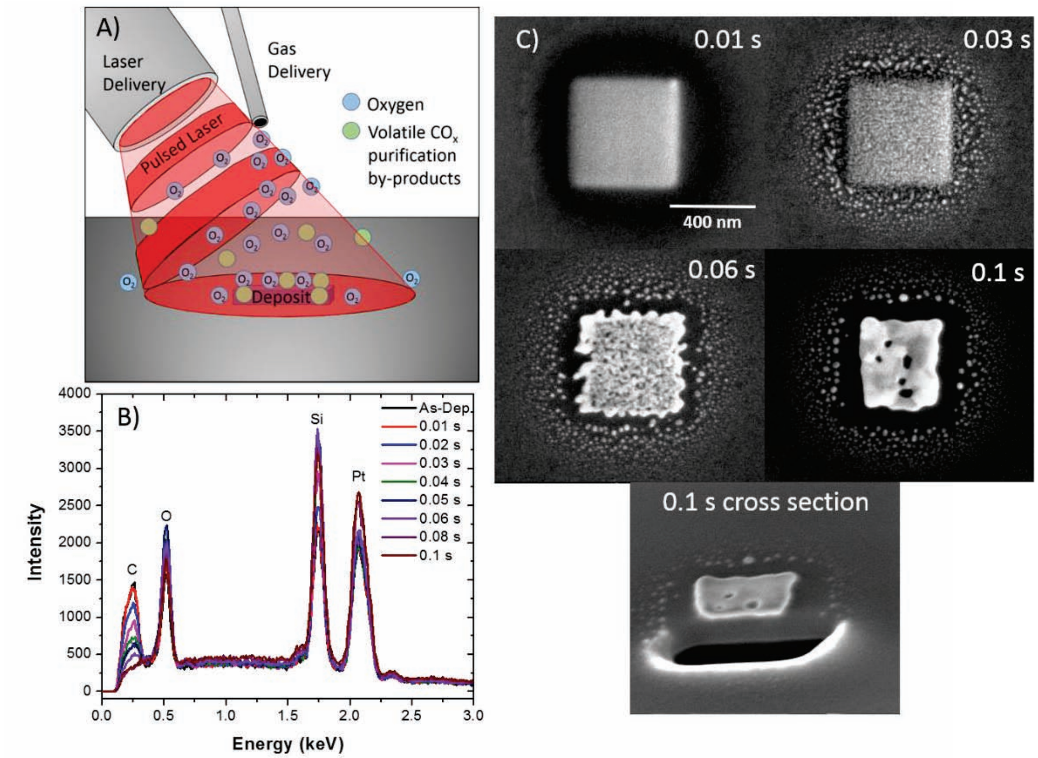

***Figure 1**: a) Schematic of the laser annealing setup with approximately 100 µm laser spot size under O_2 flow. b) EDS measurements of a ~ 140 nm thick PtC_5 EBID deposit annealed with 100µs pulses at 0.1% duty cycle as a function of exposure times. c) Images of laser annealed patterns at different exposure times. The deposit annealed for 0.1s exposure time was also cross sectioned and pictured here.*