Novel Platinum Precursors for Focused Electron Beam Induced Deposition: $PtCl_2(CO)_2$ and $PtBr_2(CO)_2$

Aya Mahgoub, C.W Hagen
Delft Univ. Technology, Dept. ImPhys, Lorentzweg 1, 2628CJ Delft, Netherlands
M.I.M.A.Mahgoub-1@tudelft.nl

Rachel Thorman, D. Howard Fairbrother
Johns Hopkins, Department of Chemistry, Baltimore, MD 21218, USA

Hang Lu, Lisa McElwee-White
University of Florida, Dept. Chemistry, Gainesville, Florida 32611-7200, USA

Focused electron beam induced deposition (FEBID) is a single-step gas-assisted additive lithography technique. It provides high spatial resolution fabrication of 3D structures from a precursor gas introduced into a regular scanning electron microscope (SEM). Often, the deposited structures contain unwanted fragments of the precursor molecules for which a solution may be found in the design of novel precursors that decompose into nicer fragments upon electron irradiation. Two new platinum precursors, $PtCl_2(CO)_2$ and $PtBr_2(CO)_2$ were synthesized and tested using a standard FEBID process in an SEM. Deposits from both precursors were compared to deposits fabricated from the commonly used $MeCpPtMe_3$ precursor, and also to deposits made in an ultra-high vacuum (UHV) environment[1,2]. From both precursors deposits can be grown in SEM, a first promising step for FEBID precursors (fig. 1) [3]. The growth rates were determined, revealing that $PtBr_2(CO)_2$ features a lower growth rate (~0.0035 nm^3/e^-) than the other two precursors. The growth rate of $PtCl_2(CO)_2$ (~0.045 nm^3/e^-) can be larger than for $MeCpPtMe_3$ (~0.020 nm^3/e^-) depending on the balance between electron flux and precursor flux. The composition, as determined by energy dispersive X-ray (EDX) analysis, of deposits from $PtCl_2(CO)_2$ [1] and $PtBr_2(CO)_2$ made in UHV, consisted of platinum and halogen only, with a stoichiometry of PtX_2 (X=Cl, Br). Surprisingly, deposits made in the SEM contained 50-60 at% carbon, 10-20 at% platinum, 7-10 at% oxygen and about 7 at% halogen. The high carbon content may find its origin in the CO-content in the precursor combined with the presence of hydrocarbons and water in the SEM. Summarizing, $PtCl_2(CO)_2$ and $PtBr_2(CO)_2$ can be successfully used in FEBID, but the reasons why the deposit composition is influenced by the deposition conditions still need to be unraveled.

---

[1] J. Spencer, Y-C. Wu, L. McElwee-White, and D.H. Fairbrother, Journal of the American Chemical Society 138, 9172-9182 (2016).

[2] J. A. Spencer, M. Barclay, M.J. Gallagher, R. Winkler, I. Unlu, Y.-C. Wu, H. Plank, L. McElwee-White, D.H. Fairbrother, Beilstein J. Nanotechnol. 8, 2410–2424 (2017).

[3] Mahgoub, A.; Lu, H.; Thorman, R. M.; Preradovic, K.; Jurca, T.; McElwee-White, L.; Fairbrother, H.; Hagen, C. W. Beilstein J. Nanotechnol. 2020, 11, 1789–1800. doi:10.3762/bjnano.11.161

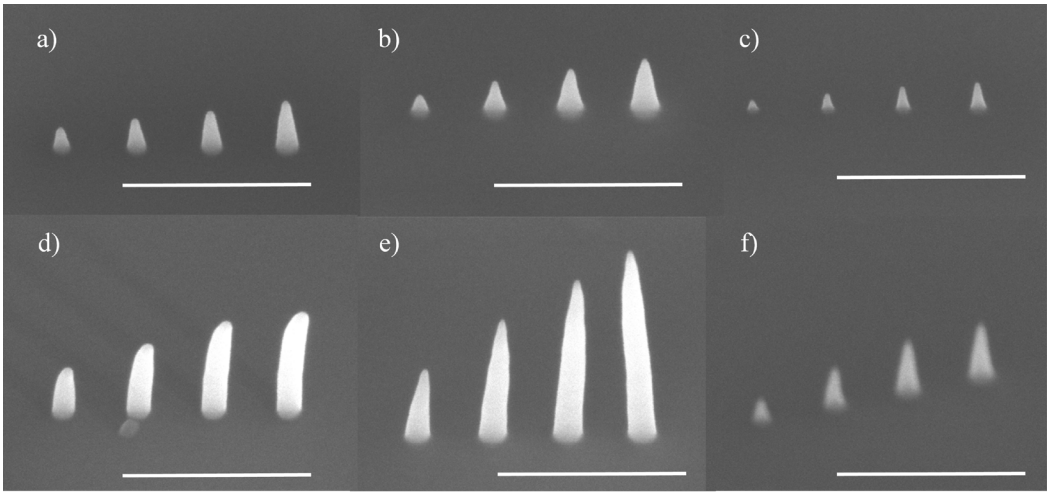

Figure 1: Comparison of pillars grown from all three precursors a) and d) $MeCpPtMe_3$, b) and e) $Pt(CO)_2Cl_2$, and c) and f) $Pt(CO)_2Br_2$. The dwell times for each pillar were 0.5, 1, 1.5 and 2 ms (left to right) and this was repeated for 200 passes. a), b), and c) are deposited at 12 pA. This corresponds to electron doses of 7.5, 15, 22.5, and 30×10^6 electrons. d), e) and f) are deposited at 38 pA, corresponding to electron doses of 24, 47, 71 and 95×10^6 electrons, respectively. The writing strategy consisted of exposure of one pillar for a certain dwell time, then blank the beam for a refresh time, ten times larger than the dwell time, then move to the next pillar. When the first pass over 4 pillars is finished, this is repeated 200 times. All scale bars are 500 nm.