



Supporting Information

## Vanadium and Manganese Carbonyls as Precursors in Electron-Induced and Thermal Deposition Processes

Felix Jungwirth <sup>1</sup>, Daniel Knez <sup>2</sup>, Fabrizio Porrati <sup>1</sup>, Alfons G. Schuck <sup>1</sup>, Michael Huth <sup>1</sup>, Harald Plank <sup>2,3</sup> and Sven Barth <sup>1,\*</sup>

- <sup>1</sup> Institute of Physics, Goethe University Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt am Main, Germany; jungwirth@physik.uni-frankfurt.de (F.J.); porrati@physik.uni-frankfurt.de (F.P.); schuck@physik.uni-frankfurt.de (A.G.S.); michael.huth@physik.uni-frankfurt.de (M.H.)
- <sup>2</sup> Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, 8010 Graz, Austria; daniel.knez@felmi-zfe.at (D.K.); harald.plank@felmi-zfe.at (H.P.)
- <sup>3</sup> Christian Doppler Laboratory for Direct–Write Fabrication of 3D Nano–Probes (DEFINE), Institute of Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria
- \* Correspondence: barth@physik.uni-frankfurt.de; Tel.: +49-69-7984-7261



**Figure S1.** Evaluation of variation in V/C ratio using V(CO)<sub>6</sub> precursor in FEBID upon changing the precursor pressure. The deposit composition is determined by EDX (11 kV). FEBID parameters include 5 kV acceleration voltage, 1.6 nA beam current, deposition area of 1.4  $\mu$ m x 1.4  $\mu$ m, 20 nm x 20 nm pitch, 1  $\mu$ s dwell-time. The deposition is carried out on Au (250 nm) / Cr (8 nm) / sapphire substrates.



**Figure S2.** Evaluation of variation in V/C ratio upon changes in the acceleration voltage for FEBID using V(CO)<sub>6</sub> precursor when the acceleration voltage for FEBID deposition is varied. The deposit composition is determined by EDX (11 kV). FEBID parameters include deposition area 1.4  $\mu$ m x 1.4  $\mu$ m, 20 nm x 20 nm pitch, 1  $\mu$ s dwell-time. The deposition is carried out on Au (250 nm) / Cr (8 nm) / sapphire substrates.



**Figure S3.** Changes in resistivity vs. electron dose for different deposition currents and variation in post-growth irradiation currents measured on of V-based FEBID material in two-probe configuration. Effect of dose on the materials resistivity is recorded *in situ* and illustrates only very minor variation with the electron beam current used for the curing.



**Figure S4.** Comparison of TEM-EDX spectra of the FEBID deposit bulk and interface between the VC<sub>1-x</sub>O<sub>x</sub> "bulk deposit" and the PtC<sub>x</sub> protection layer deposited for TEM lamella preparation.



**Figure S5.** Evaluation of compositional variation of material derived by FEBID using Mn<sub>2</sub>(CO)<sub>10</sub> precursor when the acceleration voltage for FEBID deposition is varied. The deposit composition is determined by EDX (3.5 kV). FEBID parameters include deposition area 1.4  $\mu$ m x 1.4  $\mu$ m, 20 nm x 20 nm pitch, 1  $\mu$ s dwell-time. The deposition is carried out on Au (100 nm) / Cr (8 nm) / sapphire substrates.



**Figure S6.** Changes in resistivity vs. electron dose for a Mn-based FEBID deposit in two-probe configuration. FEBID parameters include 5 kV acceleration voltage, 6.3 nA current, 20 nm x 20 nm pitch, 1  $\mu$ s dwell-time. The effect of post-growth irradiation dose on the materials resistivity is recorded *in situ* and illustrates a decrease by ~one order of magnitude.