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doi:10.1017/S1431927618012965
Microsc. Microanal. 24 (Suppl 2), 2018
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Focused Soft X-Ray Beam Induced Deposition: Recent Advances to a Novel Approach for Fabrication of Metallic Nanostructures

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Focused X-ray beam induced deposition (FXBID) is a maskless direct-write technique that combines the concepts of focused electron beam induced deposition (FEBID) and X-ray lithography (XRL). We use the focused beam of a scanning X-ray microscope (STXM) for energy-selective photo-excitation and subsequent decomposition of metal-organic precursor molecules in the gas phase [1,2]. A similar concept is maskless direct-writing by photon energy selective radiation damage of polymer substrates [3]. The process is comparable to FEBID, since radiation damage in X-ray photo-excitation is mainly caused by low-energy secondary electrons arising from Auger decays [4]. The main advantage of our new technique is the selectivity of the decomposition trigger by the incident photon energy. Therefore, it is possible to optimize deposition rates by tuning of the excitation energy according to the absorption cross-section of the precursor and, in perspective, to evaluate optimum parameters for deposition of monometallic structures from precursor mixtures. Furthermore, we target the fabrication of nanostructures with superior purity compared to FEBID by evalution of photon energy dependent fragmentation processes and plan to exploit the comparably deep penetration depth of X-rays for functionalization of porous substrates.

FXBID works by irradiation of a controlled gas flow in-between two transparent Si_3N_4 membranes forming a sealed flow cell. By focusing the monochromatic X-ray beam onto one of these membranes, we are able to deposit defined metal nanostructures from the respective precursor gas. A major advantage of using a STXM setup is the possibility of in-situ characterization of deposits in terms of thickness, purity and magnetic properties by NEXAFS and XMCD [5]. So far three precursor substances have been successfully applied for FXBID: cobalt tricarbonyl nitrosyl ($Co(CO)_3NO$), iron pentacarbonyl ($Fe(CO)_5$) and methylcyclopentadienyl manganese tricarbonyl ($MeCpMn(CO)_3$). In all cases the resulting deposits showed no proximity effects (resulting in side deposits on the Si_3N_4 membranes) which hints on a low migration length of the involved secondary electrons and a potentially high resolution of sophisticated and filigree nanostructures.

Fig. 1 shows two STXM micrographs (Co L_3-resonance) of 2D deposits from $Co(CO)_3NO$ written by FXBID with different illumination times and incident photon energies and the resulting photon energy dependent deposition rates. We observe a linear dependence of the amount of deposited material to the number of incident photons per area at each photon energy. The applied photon energies for writing have been selected as such: Co L_3- (780 eV) and O K-resonances (531 eV) from NEXAFS spectra of the deposits and respective pre- and post-edge energies. In both cases the respective resonant photon energy yields the highest deposition rate (slope of graph in Fig. 1c). Also the precursor pressure was kept

https://doi.org/10.1017/S1431927618012965 Published online by Cambridge University Press

constant (9.2 x 10^{-5} mbar), the deposition rate at the Co L_3-edge (excitation of the metal center of the precursor) is higher compared to excitation at the O *K*-edge (excitation at the ligand). This is surprising considering the respective absorption cross sections and the number of excitable atoms [2].

To investigate the photon energy dependence of the FXBID rates in more detail we performed photoionization and fragmentation studies at the GasPhase beamline at Elettra. Besides a correct determination of the resonant photon energies for the above mentioned precursors at all relevant absorption edges by calibrated NEXAFS spectroscopy, the fragmentation products were determined from time-of-flight mass spectrometry. The photon energy dependent fragmentation study shows that the major fragment upon X-ray irradiation of $Co(CO)_3NO$ and is Co^+. This suggests a comparably high rate of fragmentation and the principle possibility to generate very clean deposits by FXBID. We also find the highest degree of fragmentation (intensity of Co^+ vs. all other Co-containing fragments) at the O *K*-edge [6].

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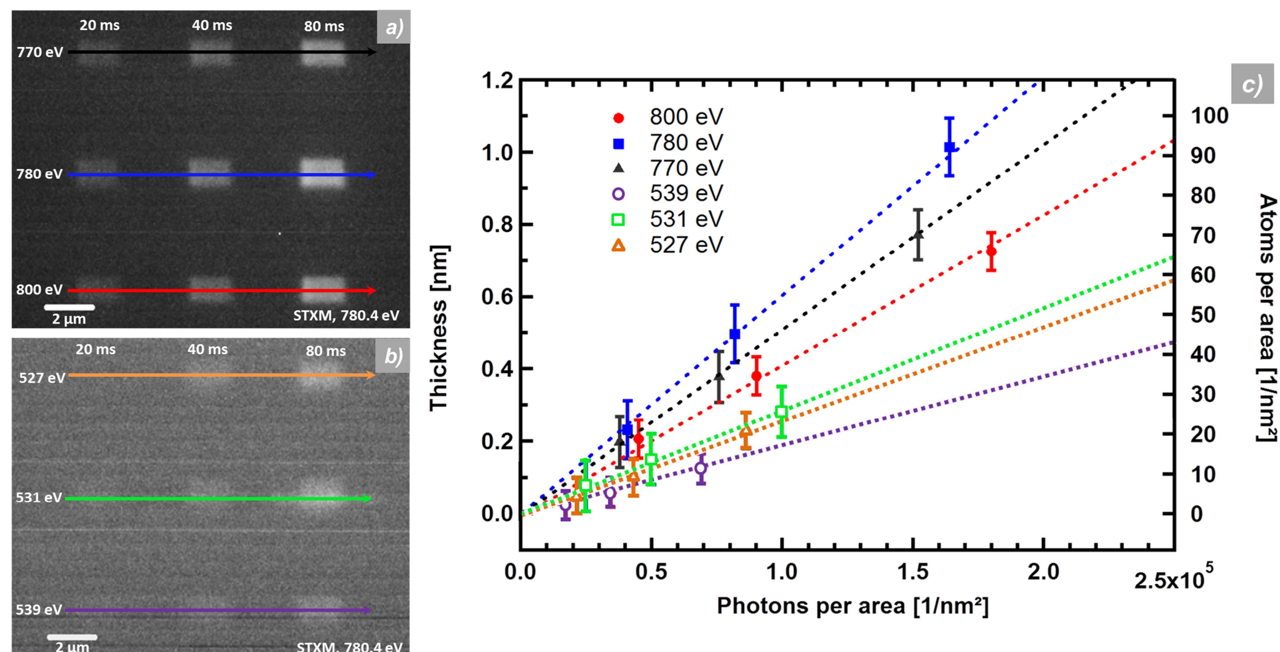

Figure. 1. STXM micrographs depicting deposits from $Co(CO)_3NO$ fabricated by FXBID at the Co L_3-edge (a) and at the O *K*-edge (b). (c) Amount of deposited material vs. number of incident photons derived from (a) and (b) depicting the respective deposition rates.

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