

Focused Electron Beam Induced Processing in ultra-high vacuum: new routes for the fabrication of clean metallic nanostructures and the reduction of proximity effects

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With the availability of localized electron probes, e.g., in scanning electron microscopy (SEM), it became possible to apply electron induced processes on the nanometer scale. Thus in Focused Electron Beam Induced Processing (FEBIP) the generation of extremely small, pure nanostructures can be targeted with lithographic control.^{1,2} The most prominent FEBIP technique is Electron Beam Induced Deposition (EBID) in which adsorbed precursor molecules are locally dissociated by the impact of the electron beam leaving a deposit of the non-volatile dissociation products on the surface.¹ Currently we were able to expand the family of FEBIP techniques with the exploration of Electron Beam Induced Surface Activation (EBISA).²⁻⁶ Thereby, in a first step, the chemical properties of the surface itself are modified via the e-beam such that it becomes active towards the decomposition of certain precursor molecules. In a second step the surface is exposed to the precursor which decomposes at the preirradiated areas and eventually continues to grow autocatalytically (AG) (Fig. 1). We demonstrate the feasibility of FEBIA with $\text{Fe}(\text{CO})_5$ for different oxide surfaces, e.g. silica (Fig 2)³ and $\text{TiO}_2(110)$ ⁴ and expand it to porphyrin layers on $\text{Ag}(111)$ ⁵ and even surface-anchored metal-organic frameworks. In addition the EBISA process is also not limited to the precursor $\text{Fe}(\text{CO})_5$ but works also for example for $\text{Co}(\text{CO})_3\text{NO}$.⁶ With our specific “surface science” approach to FEBIP, i.e. to work in an ultra-high vacuum environment, we are able to fabricate basically pure metallic deposits.²⁻⁶ One interesting aspect of EBISA is the separation of electron irradiation and deposit formation and thus the absence of proximity effects due to forward scattering since no deposit is formed during electron irradiation. Within this approach the deposition of massive metal structures can be realized with longer autocatalytic growth times instead of larger electron doses which also contributes to reduce proximity effects. In addition it appears that organic layers as substrates are suitable to reduce proximity effects due to effective decoupling of low energy secondary electrons. The underlying physical/chemical processes and in particular the potential for applications of EBISA will be discussed.

¹ a) van Dorp, W. F.; Hagen, C. W., *J. Appl. Phys.* 104, 081301 (2008); b) Utke, et al., *J. Vac. Sci. Technol. B*, 26, 1197 (2008); c) S. J. Randolph et al., *Crit. Rev. Solid State Mater. Sci.* 31, 55 (2006)

² H. Marbach, *Applied Physics A*, 117, 987 (2014).

³ a) M.-M. Walz et al., *Ang. Chem. Int. Ed.*, 49, 4669 (2010) and b) *PCCP*, 13, 17333 (2011), c) *App. Phys. Lett.*, 100, 053118 (2012).

⁴ F. Vollnhals et al., *J. Phys. Chem. C*, 117, 17674 (2013)

⁵ F. Vollnhals et al., *Langmuir*, 29, 12290 (2013)

⁶ F. Vollnhals et al., *Beilstein J Nanotech.* 5, 1175(2014)

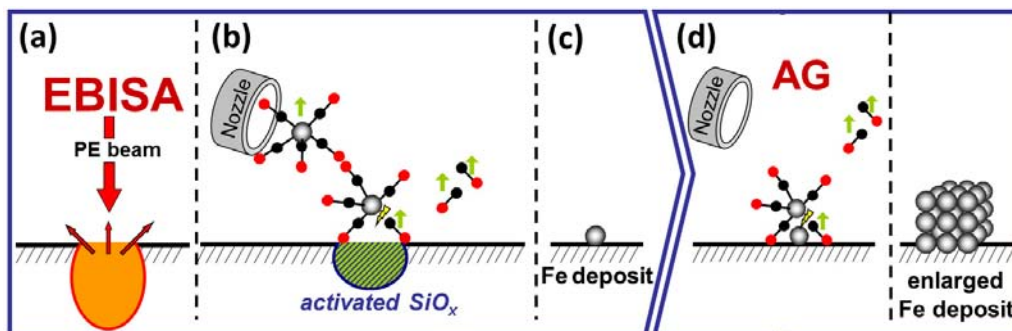


Fig. 1 (a)-(d) Scheme of the two step EBISA process with subsequent autocatalytic growth (AG).

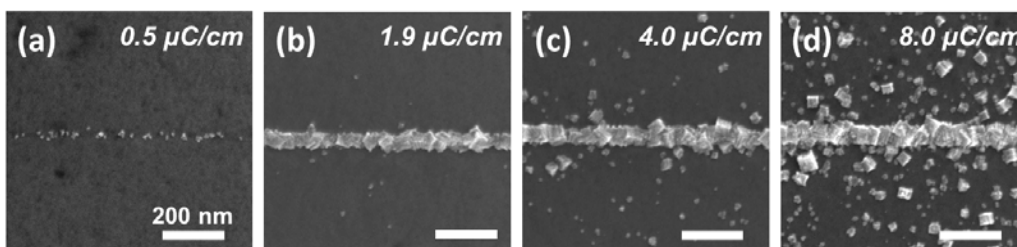


Fig. 2 (a)-(d) Scanning electron micrographs of EBISA deposits from Fe(CO)₅ on 300 nm SiO_x on Si. The electron doses are indicated. After the electron beam irradiation the surface was exposed to Fe(CO)₅ at a background pressure of 3.0×10^{-7} mbar for 4.5 h at RT.

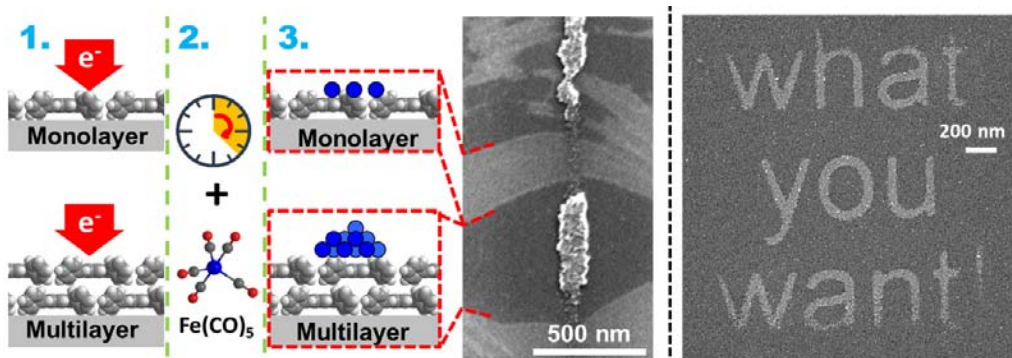


Fig. 3 Left side: Scheme and SEM image of FEBIA on porphyrin layers on Ag(111). The process is much more effective on the bilayer than on the monolayer as evidenced by the massive Fe deposits on the multilayer in the SEM micrograph. Right side: Fe deposits on an oxide surface fabricated with EBISA demonstrating the ability to draw nanostructures with lithographic control.