Addressing the Fabrication of Titanium Oxide Nanostructures by Electron Beam Induced Deposition

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Electron Beam Induced Deposition (EBID) has recently attracted considerable attention as a maskless nanofabrication tool, e.g. as main technique in state-of-the-art repair tools for UV-lithography masks. In EBID a focused electron beam is used to locally dissociate adsorbed precursor molecules. This leaves a localized deposit of non-volatile decomposition products, while volatile species are pumped off. In many applications, the fabrication of metal nanostructures is targeted with organometallic precursor molecules. Ideally, the deposit then consists of the pure metal, while the organic residues are volatile. However, unintended co-deposition of organic parts of the precursor itself and/or of residual gases from high-vacuum environments is a common drawback of the technique and hampers the fabrication of pure metallic EBID structures. In our "surface science" approach to EBID, i.e. working in ultra-high vacuum (UHV), we ensure well defined conditions and a clean environment. This route proved indeed to be successful to fabricate clean (> 95 %at.) iron nanostructures from $Fe(CO)_5$ on Rh(110) and Si(100) samples.[1,2]

Herein, we explore the more complex titanium tetraisopropoxide (TTIP) molecule as precursor for the fabrication of TiO_x nanostructures. EBID in UHV does not yield pure TiO_x deposits but TiC_xO_y composite. To remove the carbon contamination, the structures were subjected to annealing in oxygen atmosphere, which results in the growth of pure TiO_x nanocrystals.[3] Mild Ar ion milling prior to annealing in oxygen removes unintended electron proximity effect-induced deposits, which yields spatially more defined crystal growth (Fig. 1).

Furthermore, we considerably expanded the EBID technique to the fabrication of layered nanostructures by the consecutive use of two precursor gases: In the first step, an iron line was deposited with $Fe(CO)_5$, which in the second step was selectively covered with a thin capping layer of TiC_xO_y using TTIP as precursor gas (Fig. 2). Interestingly, the ultra-thin capping layer prevents the oxidation of the iron structures under ambient conditions. In summary, we present a procedure to locally fabricate clean TiO_x nanocrystals and indicate a route to reduce the size of the deposits by post treatment procedures.
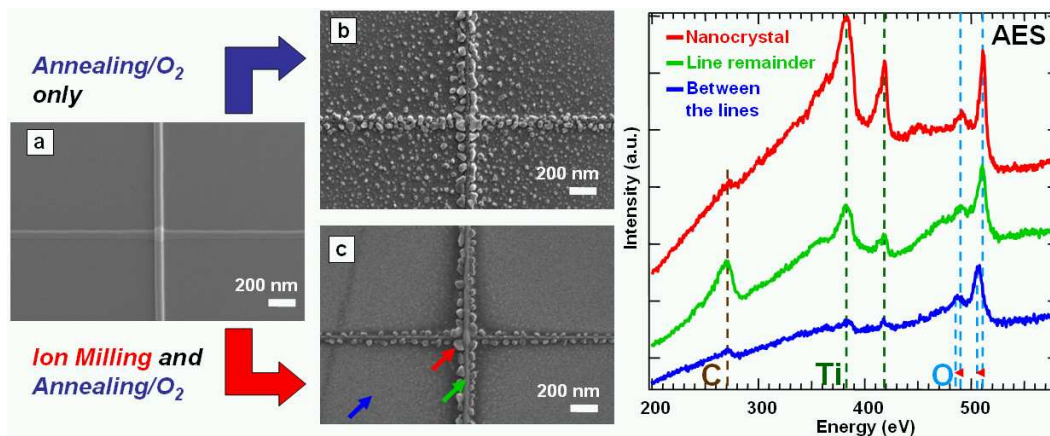
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[1] T. Lukasczyk, M. Schirmer, H.-P. Steinrück, H. Marbach, Small **4**, 841 (2008).

[2] T. Lukasczyk, M. Schirmer, H.-P. Steinrück, H. Marbach, Langmuir **25**, 11930 (2009).

[3] M. Schirmer, M.-M. Walz, F. Vollnhals, T. Lukasczyk, A. Sandmann, C. Chen, H.-P. Steinrück and H. Marbach, Nanotechnology, **in press**.

Figure 1: *TiC$_x$O$_y$ line structures on Si(100).* The as deposited lines (a) were subjected to an annealing cycle (T$_{max}$ ~1000 K) in oxygen (p=3x10^{-7} mbar) with (c) and without a prior ion milling cycle (b). In both cases the growth of crystallites is observed. Comparison of (b) and (c) shows that proximity effects can be overcome by ion milling. Auger electron spectroscopy reveals that the crystals are more or less pure TiO$_x$ (right hand side).
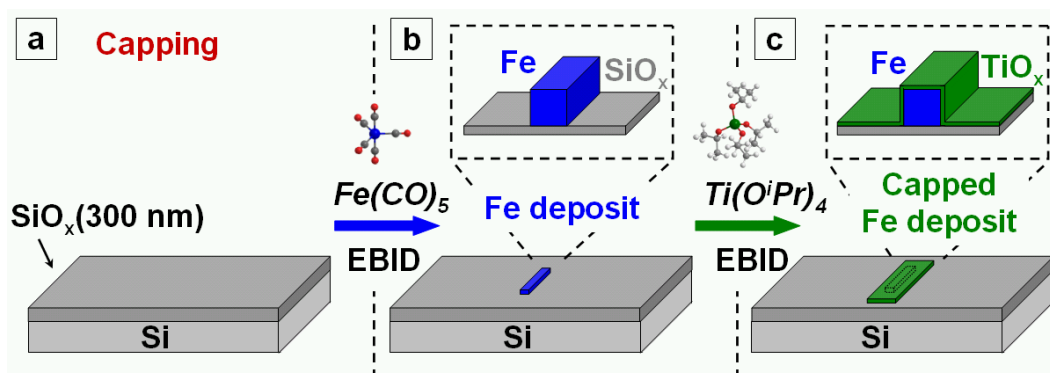
Figure 2: *Fabrication and capping of Fe deposits.* In a first step, a substrate, e.g. 300nm SiO$_x$ on silicon (a), is used as a support for EBID of iron nanostructures from iron pentacarbonyl (b). In a second step, the iron structures are selectively capped with a thin (2-3 nm) EBI deposit of TiC$_x$O$_y$ using titanium tetraisopropoxide as a precursor (c). The capping layer prevents the oxidation of the iron nanostructures.