Selective Fabrication of Pure Titanium Oxide Nanocrystals via Electron-Beam Induced Deposition in Ultra-High Vacuum

M. Schirmer, T. Lukasczyk, M.-M. Walz, F. Vollnhals,
C. Chen, H.-P. Steinrück and H. Marbach

*Lehrstuhl für Physikalische Chemie II, Department Chemie und Pharmazie, and Interdisciplinary Center for Molecular Materials (ICMM),
Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany,*
marbach@chemie.uni-erlangen.de

The mask-less technique 'electron-beam induced deposition' (EBID) is a potential tool to realize the fabrication of nanostructures with arbitrary shape and well defined chemical composition. By utilizing a highly focused electron-beam, e.g. from a scanning electron microscope, adsorbed precursor molecules are locally cracked resulting in the deposition of the non-volatile fragments.
The novel aspect of our particular 'surface science' approach is to apply the EBID process under ultra clean conditions, i.e. in an ultra-high vacuum (UHV) environment with a base pressure in the low 10^{-10} mbar regime. This allows to guarantee reproducible conditions and to overcome the hitherto existing limitation concerning the rather poor cleanliness of the deposits, as we have demonstrated for the system $Fe(CO)_5$ on Si(001)[1].
In this work, we report the generation of titanium oxide nanostructures on Si(111) and Si(100) samples fabricated with the precursor titanium(IV) tetraisopropoxide (TTIP). The structures with lithographically controlled shapes are continuous in shape and slightly contaminated with carbon (attributed to the dissociation of the large isopropoxyl ligands). By applying different post treatments we were able to enhance the purity and change the morphology of the deposits. Thermal heating of the sample and applying oxygen as reactive gas resulted in the generation of clean titanium oxide nanocrystals (see Fig. 1 and 2). A problem commonly associated with EBID is the unintended deposition next to the area directly exposed to the primary electron-beam due to proximity effects. Moderate ion sputtering before the annealing/oxygen dosage step proved to be effective to confine the titanium oxide nanocrystal formation (see Fig. 1). We will present SEM-movies of the formation of the TiO_x nanocrystals acquired *in situ* and local Auger spectra of the latter, evidencing the purity of the structures (see Fig. 2).
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1 T. Lukasczyk, M. Schirmer, H.-P. Steinrück and H. Marbach, Small **4**, 6 (2008).

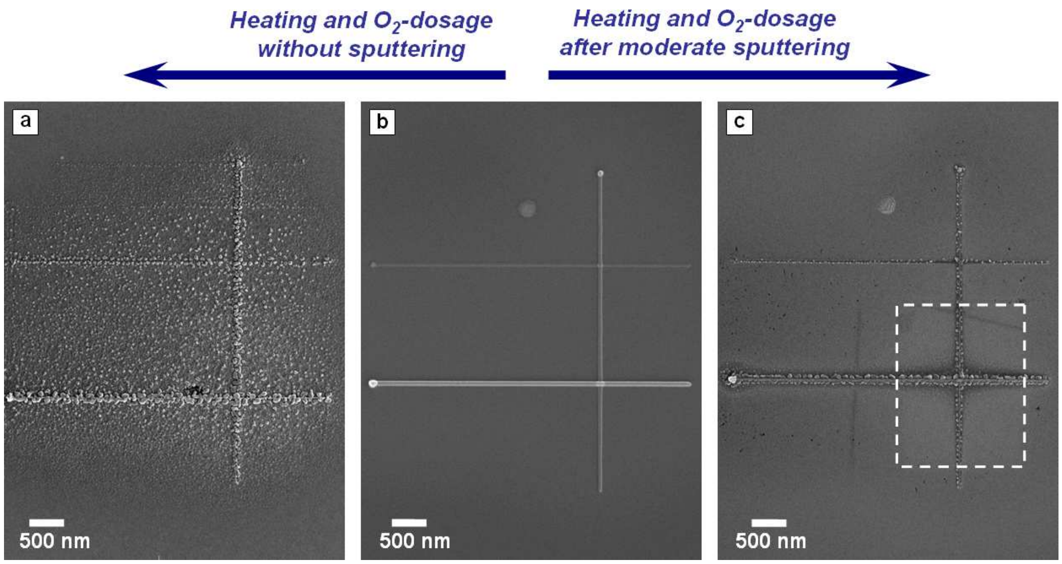

Fig. 1: Three SEM micrographs: a) TiO_x nanocrystal formation on a structure shown in b) by heating and applying O_2 without sputtering the sample before; b) Original lines fabricated via EBID; c) Confined TiO_x nanocrystal formation by moderate sputtering the sample before applying the post treatment steps.

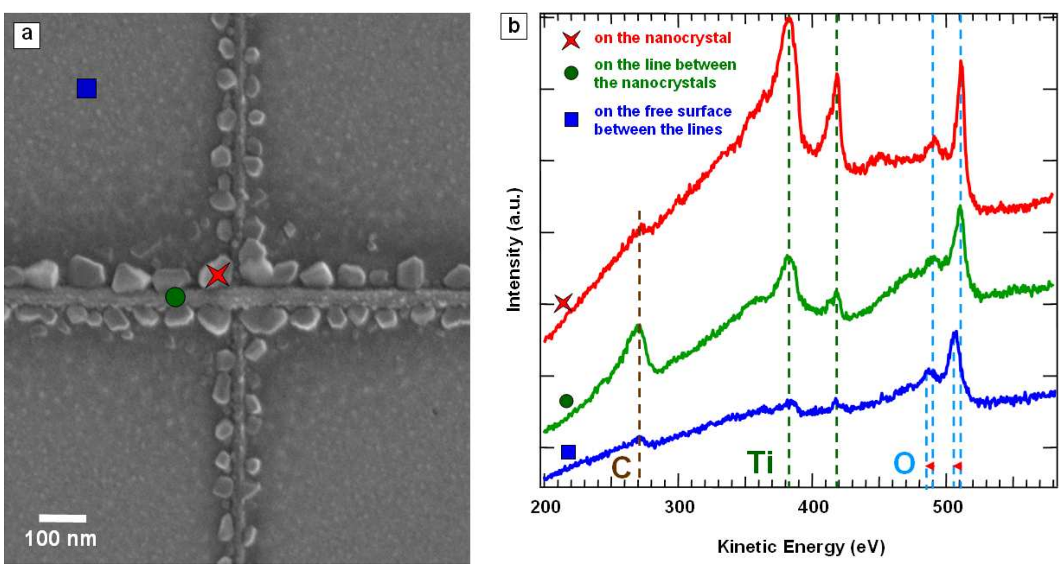

Fig. 2: AES Characterization: a) SEM micrograph at the indicated position in Fig. 1 c); b) Corresponding local Auger spectra on selected positions.