Investigation and Utilization of Oxide Surfaces in FEBIP Techniques for Nanofabrication

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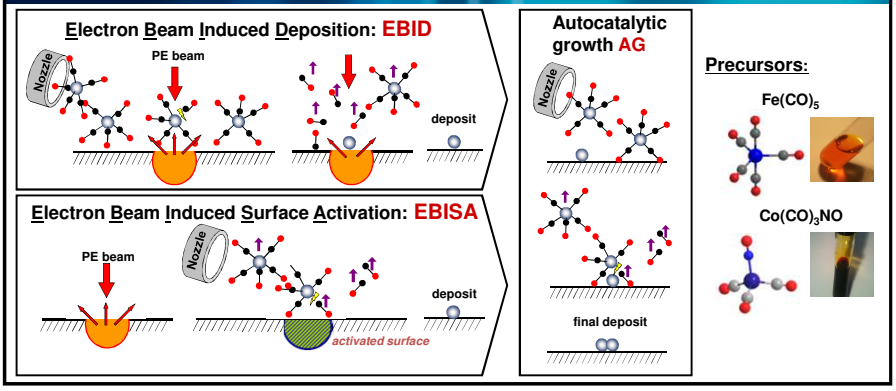
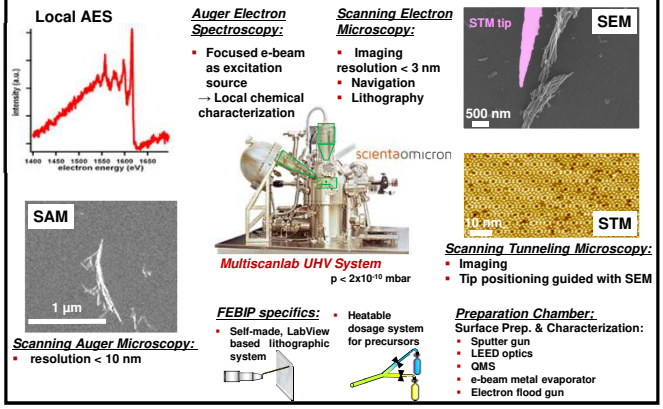
Abstract

Focused Electron Beam Induced Processing (FEBIP) refers to a number of techniques to use a focused electron beam in combination with certain precursor molecules for the controlled fabrication of arbitrarily shaped nanostructures. In our group, a deposit of the non-volatile dissociation products of adsorbed precursor molecules can be obtained either by electron beam induced deposition (EBID) or electron beam induced surface activation (EBISA) [1]. A highly focused electron beam is used to directly modify the adsorbed precursor molecules (EBID) or to locally modify the substrate in the absence of precursor molecules (EBISA) under ultra-high vacuum (UHV) conditions at room temperature. In the corresponding experiments, EBID and EBISA were conducted with two precursor molecules, iron pentacarbonyl (Fe(CO)5) and cobalt tricarbonyl nitrosyl (Co(CO)3NO) on the corresponding surfaces. While EBID can be used on most surfaces, EBISA requires a surface that can potentially be activated by the electron beam. Such surfaces are for example oxides like SiOx, or MgO, but also some organic materials can be activated [1-3]. In the corresponding experiments with the precursors Fe(CO)5 and Co(CO)3NO, we observed diverse catalytic processes on different TiO_2 surface terminations, autocatalytic growth and decomposition on previously deposited structures. We will present and discuss the corresponding observations, e.g., the partially very different chemical sensitivities of the two precursors [4]. Along with the presentation of these results, we will also demonstrate our preliminary results on Cobalt oxide as a novel oxide surface for FEBIP processes and in particular how to exploit the findings for the improvement of FEBIP.

Methods



Instrumentation



FEBIP on TiO_2(110) 1×1

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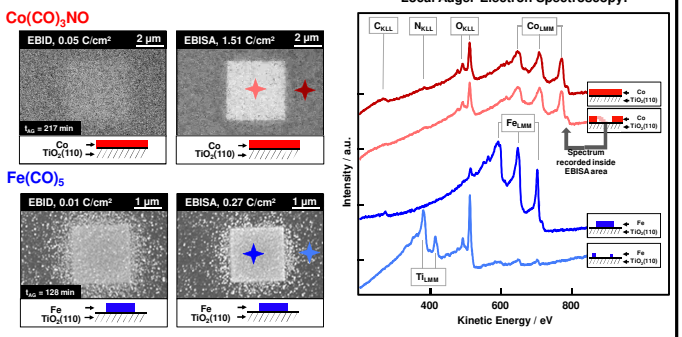
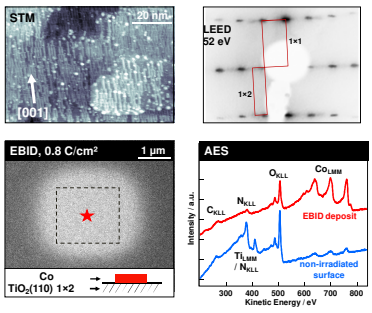
- The formation of a thick Co film and minor unselective bcc-Fe deposit on non-irradiated surface.
- EBISA with $Fe(CO)_5$; autocatalytic growth of pure, crystalline Fe (95%); but also high amount of undesired deposits due to proximity effects occur!
- TiO_2(110) 1×1 is catalytically active toward the decomposition of $Co(CO)_3NO$



- FEBIP with $Fe(CO)_5$ on TiO_2(110) 1×1 is highly selective.
- Decomposition of $Co(CO)_3NO$ consisting of ~ equal parts of Co and O, as well as very minor amounts of C and N.

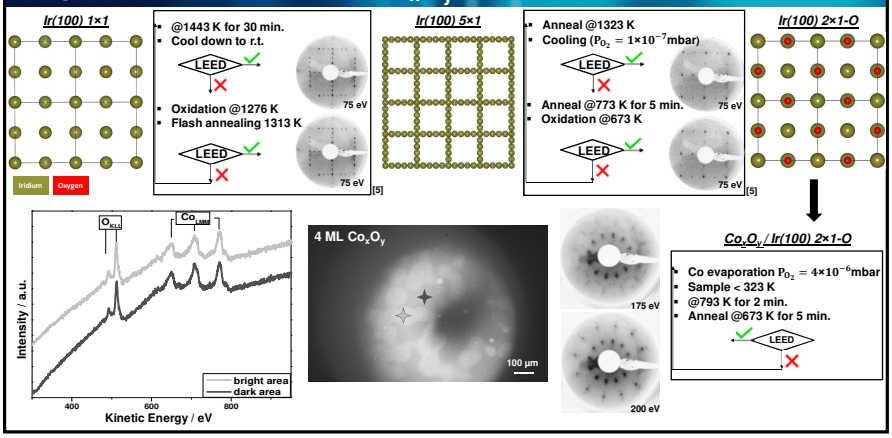
FEBIP on TiO_2(110) 1×2

FEBIP on TiO_2(110) 1×2



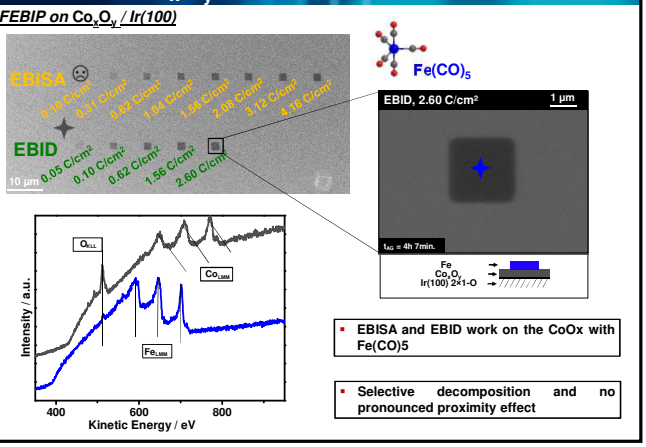
- In contrast with TiO_2(110) 1×1, unselective decomposition of $Fe(CO)_5$ on TiO_2(110) 1×2 reconsturcted surface!
- Selectivity also depends on surface reconstruction
- A more or less subtle surface modification can be sufficient to quench the catalytic activity of the latter.
- EBID with $Co(CO)_3NO$ on TiO_2(110) 1×2 is spatially selective in contrast to the 1x1 surface.

Preparation Procedure of Co_xO_y on Ir (100)



FEBIP on Co_xO_y / Ir (100)

FEBIP on Co_xO_y / Ir(100)



- EBISA and EBID work on the CoOx with Fe(CO)5
- Selective decomposition and no pronounced proximity effect

Summary

- „Inversed selectivity" on TiO_2(110) 1×2 for $Co(CO)_3NO$ and $Fe(CO)_5$
- Surface reconstructions can play a role in the FEBIP process due to their catalytic activity
- First time shown that Co_xO_y is possible for FEBIP approaches with $Fe(CO)_5$
- EBISA & EBID with $Fe(CO)_5$; autocatalytic growth of pure Fe (> 95%) on Co_xO_y / Ir(100) sample.

Comparing catalytic selectivity for two precursors

Substrate/Surface	$Fe(CO)_5$	$Co(CO)_3NO$
Ag(111) / Rh(110)	Unselective catalytic decomposition	Data not available
Si(100) 2×1	No catalytic activity FEBID possible	Unselective catalytic decomposition
SiO_x / SURMOF HKUST-1	EBISA possible	No catalytic activity FEBID possible
TiO_2(110) 1×1	EBISA possible	Unselective catalytic decomposition
TiO_2(110) 1×2	Unselective catalytic decomposition	EBISA possible
2HTPP (thin layer)	EBISA possible	EBISA possible

Literature

[1] Marbach, H., Appl. Phys. A, **117**(3): p. 987-995 (2014).
[2] Walz, M.-M., *et al.*, Angew. Chem. Int. Ed., **49**(27): p. 4669-4673 (2010).
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[5] Heinz, K., *et al.*, Journal of Physics: Condensed Matter, **25**(17), 173001 (2013).

Acknowledgements

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