Doctoral thesis assessment.

Title of thesis:
Study of novel precursors for Focused Electron Beam Induced Deposition of Metal Nanowires

Doctoral candidate submitting the thesis:
Mr. Jakub Mateusz Jurczyk..

Reykjavík November 8, 2021

To whom it may concern,

The PhD theses work of Mr. Jakub Mateusz Jurczyk addresses thematic of significant complexity. His research work addresses parameter and process optimization in focused electron induced deposition (FEBID), an emerging nanofabrication method with significant potential in prototyping and production of functional three-dimensional nanostructures.

The main part of the thesis concerns studies of novel FEBID precursor molecules intended for silver, ruthenium and gold depositions. In total, systematic deposition studies on nine precursors are conducted within the framework of this thesis. The studies are thorough and a considerable parameter space is considered. This work alone, or even a part of it, would in my opinion be sufficiently novel and significant to constitute a good and defendable PhD thesis. However, in his work Mr. Jurczyk also delivers meaningful FEBID modeling work and contributes to the introduction and development of new characterization and analytical methods.

The extent and the quality of Mr. Jurczyk's work are excellent and it ranks among the better PhD research works I have evaluated.

The thesis is at large well-written, scholarly and concise, without sacrificing details of significance. It is constructed in a conventional, accessible form with a problem statement, an introduction and an experimental section proceeding the presentation and discussion of the research conducted. The thesis is then concluded with a summary and outlook section.

Dunhagi 5
107 Reykjavik, Iceland
Tel. +354 525 4700
Web. von.hi.is/rvd

The Introduction addresses the general principles of FEBID and related nanofabrication techniques, gives an adequately comprehensive overview of precursor compounds used in this technique and their performance, and discusses the nature of the physical processes behind the deposition process. These sections address the complexity of the process and underline the problem statement. Following these sections, a comprehensive discussion on simulation parameters and FEBID modeling approaches is delivered and following that, the main approaches for characterization of deposits and precursors are given.

Overall the introduction is well structured and the state-of-the-art is adequately presented with passable literature reference given.

The experimental section offers a thorough description of the experimental approaches applied including problematic, deviation from standard operation conditions and expansion or adaption of the methods to the problems at hand. Noticeably, the work conducted within the current PhD thesis, required the mastering of a broad range of experimental techniques, including Scanning and transmission electron microscopy, focused electron beam induced deposition, energy and wavelength dispersive X-Ray analysis, atomic force microscopy, four-point resistivity measurements, in situ mass spectrometry and conventional as well as vacuum themogravimetry.

The mastering of these techniques and their application for reliable data acquisition is not trivial and Mr. Jurczyk shows in the experimental section as well as in the following presentation and discussion of his research that he masters these techniques well and is capable of approaching them and the associated data analysis in critical manners.

In the results and discussion section Mr. Jurczyk presents his research on three groups of novel FEBID precursors; silver carboxylates with different side chains, both aliphatic and perfuorinated, two ruthenium bromo carbonyl complexes from which one also contains an allyl group and two gold(I) hetrocyclic carben complexes with different chain length N-substitution.

Five silver carboxylates were studied. A thorough and comprehensive analysis on the thermal properties of these compounds is offered with respect to their sublimation and decomposition temperatures. This was carried out both through conventional TGA and vacuum TGA and is compared to the performance of these compounds in FEBID at differed

Sæmundargötu 6
101 Reykjavík
Sími 525 4000
Fax 552 1331
hi@hi.is
www.hi.is

GIS and deposition temperatures. Systematic single spot, area and line/wire depositions were carried out as well as deposition on different substrates suitable for different analytical approaches. The deposits were systematically assessed with respect to composition and morphology, including spatial composition, i.e., differences in the center and the halo region of deposits. Temperature dependent resistivity measurements were carried out on wires deposited from each precursor, and in context to the application of silver nano-structures in plasmonics, pillar deposition was probed with two of the silver precursors.

Similar to the silver precursor, FEBID with $Ru(\eta^3\text{-}C_3H_5)(CO)_3Br$ was systematically studied on different substrates and deposits were characterized with respect to their composition, morphology, resistivity and suitability for the deposition of higher aspect ratio structures. For $Ru(CO)_4Br_2$, on the other hand the focus was mainly on composition control under different beam currents and stage temperatures. The results are compared to earlier surface science and gas phase studies. Finally this section of the thesis work also comprises systematic studies on two novel gold(I) precursors. These studies were conducted in similar way as the studies discussed here above with depositions created on different surfaces, and morphology and composition characterization under different deposition conditions.

The approach to these experiments and the overall conduct is systematic and well suited to revile the properties critical for the evaluation of the performance of these precursors. The analysis and discussion is knowledgeable and critical and the data and its presentation give valuable insight into the performance of these materials and also indications of potential paths for further improvement on FEBID precursors. In my opinion the presented deposition and characterization studies on these nine novel precursors would alone justify the defense of this PhD thesis and rank it as excellent work.

In addition to the studies on the performance of these novel precursors the candidate contributed to the development and did experimental work on a new analytical FEBID-MS setup and contributed to further development of FEBID modeling approaches.

With the FEBID-MS setup the candidate measured, in situ mass spectra of charged fragments formed in the FEBID process with $Ru_3(CO)_{12}$, $Ag_2(\mu\text{-}O_2CC_2F_5)_2$, $Cu_2(\mu\text{-}O_2CC_2F_5)_4$ and $W(CO)_6$. These experiments are preliminary and the discussion and interpretation is at large qualitative. However these experiments and the data presented, clearly demonstrate the potential of this new approach. In fact, having read that section, I have some ideas of a

Sæmundargötu 6
101 Reykjavík
Sími 525 4000
Fax 552 1331
hi@hi.is
www.hi.is

collaborative project that would address core questions in the deposition process that would be worth pursuing.

In his approach to the modeling of the FEBID process Mr. Jurczyk extends the characteristic rate maps by inclusion of a resolution parameter and by considering diffusion. Separately he also extends the current description by introducing two differential terms describing ligand deposition, thus extending the model towards composition description. The predictions of the deposition model are then compared to experimental deposition of $Cr(CO)_6$.

The thesis covers a broad scope, including a core element that suffices as a stand alone thesis and two elements, experimental and theoretical, which both have novel components and open the door for further research, which in turn would pose problems worth addressing further through individual PhD projects. The work is novel and significant and provides original solutions to scientific problems. Mr. Jurczyk is clearly knowledgeable in the field addressed and shows innovation in his approaches, without sacrificing the systematic element needed in addressing multi parameter problems, such as the once at hand in his thesis work. Further, the work of Mr. Jurczyk has contributed to 11 publications, partly in top ranking journals, which a clear testimony of the quality and extent of his work.

This work is of high standard and should be accepted for further procedures foreseen on the path towards the award of a PhD. Furthermore, justified by my assessment here above, I recommend that this doctoral dissertation be awarded with distinction.

Yours sincerely,

Prof. Dr. Oddur Ingólfsson

Department of Chemistry, University of Iceland
Science Institute, Dunhaga 3, 107 Reykjavík, Iceland
Tel.: +354-5254313, Fax.: +354-5528911.

e-mail; odduring@hi.is