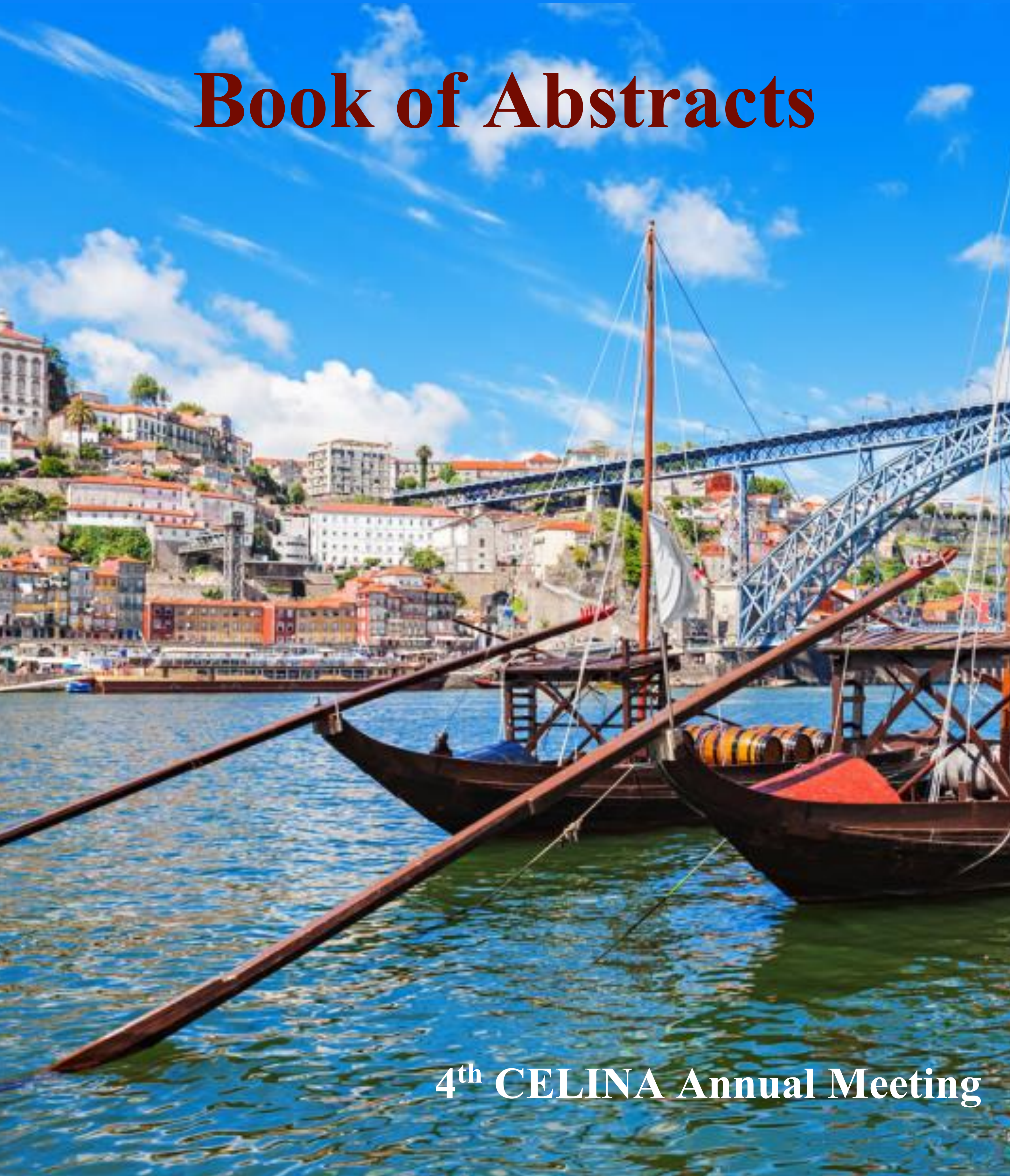
CELINA 2017

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Chemistry for ELectron-Induced NAnofabrication (CELINA)
COST Action CM1301

Porto 13-16 September 2017



Book of Abstracts

4th CELINA Annual Meeting

Chemistry for Electron-Induced Nanofabrication (CELINA) COST Action CM1301
Porto, Portugal
13-16 September, 2017

Edited by:
Filipe Ferreira da Silva
Gonçalo Magalhães-Mota

Chemistry for Electron-Induced Nanofabrication (CELINA)

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Editorial

Dear Colleagues,

Welcome to Porto and CELINA 2017, the 4th and the last annual meeting of **CELINA Chemistry for ELectron-Induced Nanofabrication**, COST Action CM1301. CELINA 2017 permits to achieve a very privileged forum of sharing and developing our scientific expertise on current aspects of Electron induced reactions of FEBID precursors, synthesis of novel FEBID precursors and Application of novel precursors in FEBID process. We are very pleased to host in Porto, Portugal the 4th and the last CELINA annual meeting with the participation of 70 scientists from 18 countries.

CELINA 2017 promises to be an exciting and stimulating conference with 7 topical sessions with 26 topical lectures, and XX posters providing a very privileged opportunity of scientific discussions on the scope of CELINA COST Action.

CELINA book of abstracts, newsletter front page and badges envisage the beautifulness and unique shape of Porto, through the Douro river. While Porto is at present one of the most important cities in Portugal, its beginnings do not necessarily match its current economic, cultural and tourist prestige. It is true during the Roman age, when, in fact, the entire Iberian Peninsula was dominated by the Romans, the region now known as Porto used to play an important role in the trade between Lisbon and Braga, but it was not until centuries later that Porto actually became a point of reference for the economic life of Portugal. Thus, a settlement was determined to have been founded on the north bank of the Douro River somewhere in the 4th century BC, a settlement from the name of which the contemporary name of Portugal derives: Portus Cale, later transformed in Portucale

We would like to express our gratitude to the local organizing committee, in particular to Gonçalo Magalhães-Mota, Ana Rita Pecorelli, Tiago Cunha, Emanuele Lange and Ana Cruz who worked so hard and made this meeting happen.

Last but not least, we wish you a successful meeting and a pleasant stay in Porto.

Filipe Ferreira da Silva

Paulo Limão-Vieira

Maria José Calhorda

CELINA 2017 Chairs

Porto, September 2017

General Information

REGISTRATION

The registration desk will be on the atrium of the Seminário de Vilar building from 16:00 to 19:00 on Wednesday 13th September.

VENUE FOR SCIENTIFIC PRESENTATIONS

The CELINA 2017 opening will be held on Thursday 14th July at 08:45 in Seminário de Vilar, where the lectures will take place. Poster session will be held on Thursday 14th September from 16:00 to 19:00 in the atrium of the building.

ORAL PRESENTATIONS

Room is equipped with desktop computer. Speakers are recommended to bring their presentations in ppt, pptx or PDF format on a USB pen drive. Speakers should upload their presentations in advance. Speakers who want to use their Mackintosh should bring DVI-VGA or DisplayPort-VGA adapter.

POSTER PRESENTATIONS

Posters should fit A0 size (84cm x 118.8cm / 33inch x 46.8 inch) suitable for the boards.

BADGES

Please have your badge all the time.

WELCOME RECEPTION AND CONFERENCE DINNER

The welcome reception will be held in on Wednesday 13th September at the atrium of Seminário de Vilar building and the conference dinner on Friday 15th September at "Árvore" restaurant.

POSTER PRIZE

The Scientific Committee together with all participants will award a poster prize to the best CELINA 2017 poster. The winner will be announced and awarded during the conference dinner.

INTERNET ACCESS

There is free Wi-Fi internet access in the rooms and in the atrium of the Seminário de Vilar building. Details will be provided at the conference.

MEALS

Lunch and coffee break are provided on 14th, 15th and 16th September.

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Wednesday 13th September

14:00 – 19:00	REGISTRATION AND WELCOME RECEPTION (Seminário de Vilar, Porto)

Thursday 14th September

08:30 – 09:00	**Opening Remarks**
	CELINA overview and synthetic perspectives
09:00 – 09:20	Chair: Kees Hagen
	Petra Swidereck (*University of Bremen*)
	“COST Action CM1301 – CELINA: What has been achieved and what lies ahead?”
	Novel developments in FEBID and beyond
09:20 – 09:50	**José Maria de Teresa** (*University of Saragoza)*
	“Novel developments in FEBID for magnetic materials”
09:50 – 10:20	**Armin Gölzhäuser** (*University of Bielefeld*)
	“Imaging, modification and analysis of nanostructures with the helium ion microscope”
10:20 – 10:40	**Teodor Gotszalk** (*Wrocław University of Technology)*
	“Novel devices including functional FEBID structures”
10:40 – 11:10	**COFFEE BREAK**
11:10 – 11:40	**Carboxylate precursors**
	Chair Heinrich Lang
	Iwona Szymanska (*Nicolaus Copernicus University in Toruń*)
	“Overview of properties and synthetic strategies towards carboxylate FEBID precursors”
	Ivo Utke (*EMPA – Swiss Federal Laboratories for Material Science and Technology)*
11:40 – 12:00	“Gas assisted focused electron beam induced deposition with low volatility precursors”
12:00 – 12:20	**Katarzyna Madajska** (*Nicolaus Copernicus University in Toruń*)
	“Perfluorinated silver (I) carboxylate compounds for focused electron beam induced deposition (FEBID)”
12:20 – 12:50	**Lionel Amiaud** (*University of Paris-Sud*)
	“New FEBID copper precursor under high vacuum for the study of chemical processes induced by low energy electron irradiation”
12:50 – 14:00	**LUNCH**

Bimetalic precursors
14:00 – 14:30 Chair: Nigel Mason
Sven Barth (*Technical University of Vienna)*
"Synthesis of heteroleptic and metallic precursors for focused electron beam induced deposition"

14:30 – 15:00 **Oddur Ingólfsson** (*University of Iceland*)
"Electron induced fragmentation of bimetallic focused electron beam induced deposition precursors"

15:00 – 15:30 **Michael Huth** (*Goethe University)*
"Complex 3D magnetic nanostructures prepared by FEBID"

15:30 – 15:50 **Ragesh Kumar** (*University of Iceland*)
"Electron induced surface reaction of bimetal FEBID precursor molecules $HFeCo_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$"

15:50 – 19:00 **Poster Session**
COST Action CM1301 CELINA MC Meeting

Friday 15th September

Neutral excitation and dissociation
09:00 – 09:30 Chair: Oddur Ingólfsson
Juray Fedor (*Czech Academy of Sciences*)
"Neutral dissociation: review of experimental approaches"

09:30 – 10:00 **Matija Zlatar** (*University of Belgrade)*
"The role of electronic excitations in FEBID precursors"

10:00 – 10:20 **Juraj Orzsagh** (*Comenius University*)
"Electron induced fluorescence – detection of neutral fragments"

10:20 – 10:40 **Anita Ribar** (*Comenius University and University of Innsbruck*)
"The role of electron self-scavenging in aggregates of $Cr(CO)_6$"

10:40 – 11:10 **COFFEE BREAK**
11:00 – 11:40 **Novel developments in FEBID and beyond**
Chair: Armin Gölzhäuser
Gregor Hlawaczek (*Institute for Ion Beam Physics and Materials Research)*
"Nano-fabrication with the helium microscope"

11:40 – 12:10 **CELINA overview and synthetic perspectives**
Lisa McElwee-White (*University of Florida)*
"Mechanism-based design of precursors for FEBID"

12:10 – 12:50 **Discussion on future activities**
COST Action CM1301 CELINA WG Meetings

12:50 – 14:00	**LUNCH**
14:00 – 19:00	**Walking tour**
19:00	**CONFERENCE DINNER**

Saturday 16th September

09:00 – 09:30	**Process gases for deposit purification and lithography** Chair: Ivo Utke **Mostafa M. Shawarav** (*Institute of solid state electronics*) “An overview of in-situ ad ex-situ purification strategies for FEBID gold nanostructures”
09:30 – 10:00	**Anpan Han** (*Technical University of Denmark)* “Organic ices resists”
10:00 – 10:20	**Markus Rohdenburg** (*University of Bremen*) “Expanding and understanding water-assisted purification procedures: a case study of the potential FEBID precursor $(EtCp)_2Ru$”
10:20 – 10:40	**Carboxylate precursors** **Katja Höflich** (*EMPA – Swiss Federal Laboratories for Material Science and Technology*) “Direct electron beam writing of silver-based nanostructures”
10:40 – 11:10	**COFFEE BREAK**
11:10 – 11:30	**Improved control over electron-driven processing** Chair: Juraj Fedor **Janina Kopyra** (*Siedlce University)* “Low energy electron triggered fragmentation of metal acetylacetonates”
11:30 – 11:50	**Neutral excitation and dissociation** **Sylwia Ptasinska** (*University of Notre Dame*) “Instrumentation for neutral radical detection from gas-phase molecular dissociative electron attachment”
11:50 – 12:10	**Improved control over electron-driven processing** **Gian Carlo Gazzadi** (*S3 center – Nanoscience Institute)* “FEBID of W and Pt precursors at very low energy”
12:10 – 12:30	**Sascha Koch** (*University of Bielefeld)* “Amplified cross-linking efficiency of SAMs through targeted DEA for production of CNMs”
12:30 – 12:50	**Concluding remarks**
12:50 – 14:00	**LUNCH**
14:00	**Departure**

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Speaker Abstracts

T-01: COST Action CM1301 – CELINA: What has been achieved and what lies ahead?

Petra Swiderek

Chair of COST Action CM1301
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Since 2013, the European COST Action CELINA (**C**hemistry for **EL**ectron-**I**nduced **NA**nofabrication [1]) has stimulated collaborative research that aims at improving the performance of focused electron beam induced deposition (FEBID) processes. It has particularly aimed at understanding the chemistry underlying FEBID processes and at the development of novel and improved precursor molecules. CELINA has thus networked research concerned with the fundamentals of electron-driven chemistry (Working Group 1) with groups engaged in precursor synthesis (Working Group 2) and with the FEBID community (Working Group 3). This multidisciplinary effort is needed because of the many different physical and chemical aspects involved in the formation and processing of a FEBID deposit. It is the particular aim of CELINA 2017 to highlight what has been achieved during the four year duration of the Action but also to discuss future research needs and perspectives. This contribution sets the stage for these discussions by summarizing briefly the aims, strategies, and highlights of the Action.

References

[1] http://celina.uni-bremen.de/celina

T-02: Novel developments in FEBID for magnetic materials

Javier Pablo-Navarro[1], César Magén[1,2], Soraya Sangiao[1], Rosa Córdoba[2], José María De Teresa[1,2]

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The growth of functional magnetic materials is one of the successful examples of application of the FEBID technique, as reviewed in references 1 and 2 [1, 2]. In this contribution, recent progress in the development of FEBID for application in the growth of magnetic materials will be reported.

The following new aspects will be covered in the talk:

- The growth of magnetic nanowires with varying diameter [3]
- The growth of magnetic nanowires with three-dimensional shapes [4] and their mechanical properties [5]
- The growth of core-shell magnetic nanowires and nanotubes [6]
- The growth of magnetic nanospheres and nanowires on cantilevers [7]
- Purification and re-crystallization of three-dimensional magnetic nanowires [8]

The main focus of the presentation will be given to the potentiality of FEBID for the growth of tailored magnetic nanostructures as well as to their potential applications.

References

[2] J. M. De Teresa and A. Fernández-Pacheco, *Appl. Phys. A* **117** (2014) 1645–58
[3] J. M. De Teresa, A. Fernández-Pacheco, R. Córdoba, L. Serrano-Ramón, S. Sangiao and M. R. Ibarra, *J. Phys. D: Appl. Phys.* **49** (2016) 243003
[4] J. Pablo-Navarro, D. Sanz-Hernández, C. Magén, A. Fernández-Pacheco, J. M. De Teresa, *J. Phys. D: Appl. Phys.* **50** (2017) 18LT01
[5] A. Wartelle et al., arXiv:1702.02083
[6] R. Córdoba et al., submitted
[7] J. Pablo-Navarro, C. Magén, J. M. De Teresa, *Nanotechnology* **27** (2016) 285302
[8] S. Sangiao et al., submitted
[9] J. Pablo-Navarro, C. Magén, J. M. De Teresa, *manuscript in preparation*

T-03: Imaging, Modification, and Analysis of Nanostructures with the Helium Ion Microscope

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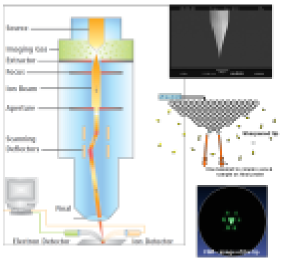
The Helium Ion Microscope (HIM) is a scanning microscope that utilizes a focused beam of helium ions to image and modify materials with high spatial resolution and chemical sensitivity [1]. A HIM can be envisioned as a scanning electron microscope (SEM) with a helium ion beam. The helium ion beam can be focused into a smaller diameter than an electron beam, and the HIM is thus capable to resolve features down to 0.25 nm. Helium ions are also more surface sensitive than electrons and they interact more strongly with matter. HIM images thus show much stronger chemical and topographical contrasts than SEM images. The HIM is further capable to image not only conductive, but also insulating samples without special treatment. This allows the investigation of unstained biomaterials and cell surfaces. When applying higher ion currents, the HIM can be also used for the modification and the milling of materials.

The presentation will contain various examples of HIM imaging and lithography. A particular focus is laid on 2D materials. 1 nm thick carbon nanomembranes (CNMs) are engineered with a controlled thickness, elasticity, conductivity and porosity [2]. HIM images provide valuable information to understand the structure of CNMs and their formation process [3]. The capability of the HIM for nanolithography of 2D materials will be shown by examples of milling CNMs and graphene, where nanopores with diameters down to 1.3 nm were fabricated [4]. HIM imaging of different carbon materials as well as of biological cells [5] will also be discussed.



Schematic of a Helium Ion Microscope (HIM): The He$^+$ ion source, realized by a metal tip sharpened in a field ion microscope to form an atomic trimer at the tip apex (Fig. from Carl Zeiss).

[1] G. Hlawacek and A. Gölzhäuser (Ed.): *Helium Ion Microscopy*, Springer-International (2016).

[2] A. Turchanin and A. Gölzhäuser: *Carbon Nanomembranes*, Adv. Mater. **28**, 6075 (2016).

[3] A. Beyer, H. Vieker, R. Klett, H. Meyer zu Theenhausen, P. Angelova and A. Gölzhäuser: *Imaging of carbon nanomembranes with helium ion microscopy*, Beilstein J. of Nanotechnol. **6**, 1712 (2015).

[4] D. Emmrich, A. Beyer, A. Nadzeyka, S. Bauerdick, J. C. Meyer, J. Kotakoski and A. Gölzhäuser: *Nanopore Fabrication and Characterization by Helium Ion Microscopy*, Appl. Phys. Lett. **108**, 16310 (2016).

[5] M. Schürmann, N. Frese, A. Beyer, P. Heimann, D. Widera, V. Mönkemöller, T. Huser, B. Kaltschmidt, C. Kaltschmidt and A. Gölzhäuser: *Helium Ion Microscopy Visualizes Lipid Nanodomains in Mammalian Cells*, Small 43, 5781 (2015).

T-04: Novel devices including functional FEBID structures

Teodor Gotszalk[1], Wojciech Majstrzyk[1] , Magdalena Moczała[1], Karolina Orłowska[1], , Andrzej Sierakowski[2], Paweł Janus, Marcus Puydinger[3], Ivo Utke[3]

[1] Wrocław University of Technology, Faculty of Microsystem Electronics and Photonics, Janiszewskiego 11/17, 50–372 Wrocław, Poland
[2] Institute of Electron Technology, Al. Lotników 32/46, 02-668 Warsaw, Poland
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Focused electron beam (FIB) and scanning electron microscopy (SEM) enable fabrication of three dimensional (3D) structures at the locations defined with single nanometer resolution. To the technologies which are based on FIB and SEM methodology belongs focused electron beam induced deposition (FEBID) making it possible to integrate various conductive and magnetic structures with micro- and nanoelectromechanical systems (MEMS and NEMS). During the presentation we will present a method of fabrication and characterization of FEBID nanogranular resistors (NGRs) fabricated basing on the platinum and cobalt precursors, which can be used as the deflection detector of silicon nitride microbridges. In our experiments we applied the thin film double clamped microstructures with platinum metallization as stable structures of resonance frequency reaching MHz. The deflection sensitivity of the NGR strain sensor was tested using a contact mode atomic force microscope, which enabled us to test the sensitivity when test deflection was smaller than 2 µm. We will also report on measurement technology enabling electrical detection of resonance microbridge behavior. Moreover characterization of magnetic cobalt FEBID nanostructures done using silicon microcantilever arrays will be described. The silicon structures are applied as mass change and force sensors, whose deflection when measured in the defined magnetic field makes it possible to describe the FEID structure properties

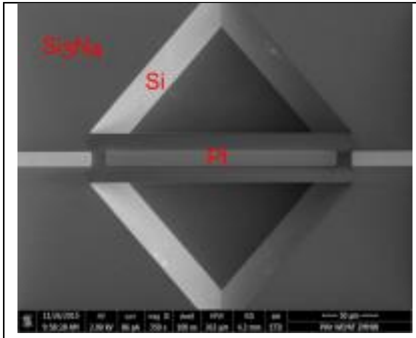

Fig. 1. Silicon nitride microbridge with platinum thin film metallization before FEBID NGR deposition.

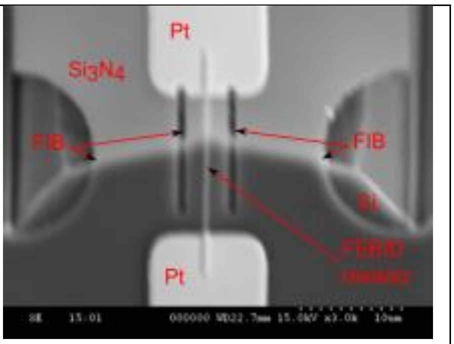

Fig. 2. Platinum FEBID NGR deposited on FIB modified silicon nitride microbridge.

Acknowledgements

Fabrication of the silicon cantilevers for testing of the cobalt FEBID nanostructures was done within the NCN OPUS 9 Grant - “Metrology of molecular interactions using electromagnetically actuated MEMS force sensors-MetMolMEMS” (Grant No. 2015/17/B/ST7/03876) and Wrocław University of Science and Technology statutory founding.

T-05: Overview of properties and synthetic strategies towards carboxylate FEBID precursors

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Compounds of semi-precious (Cu) and precious (Ag) metals constitute a topic of intensive studies because they show interesting physicochemical and structural properties and are significant for the development of nanotechnology. Focused electron beam induced deposition (FEBID) is a direct maskless nanolithography technique, based on the local dissociation of adsorbates upon the irradiation with electrons. The FEBID precursors should have the ability to generate volatile metal carriers, which are transported over a substrate, on which they decompose upon the irradiation forming the desirable material [1].

Copper and silver carboxylate compounds were applied as precursors in thermal induced chemical vapor deposition of mono- and bimetallic materials [2,3]. Carboxylates are ligands, which can form mono-, di-, and multinuclear structures because they are able to coordinate to metals as monodentates, chelates, and bridging. Moreover, the possibility of mono- and additional bridging formation influences a more complicated coordination mode and results in different space structures *e.g.* chains, sheets (Figure 1). Therefore, the secondary ligands (*e.g.* water, amines) are applied to prevent the above process. On the other hand, these molecules enable manipulating physicochemical parameters of potential precursors.

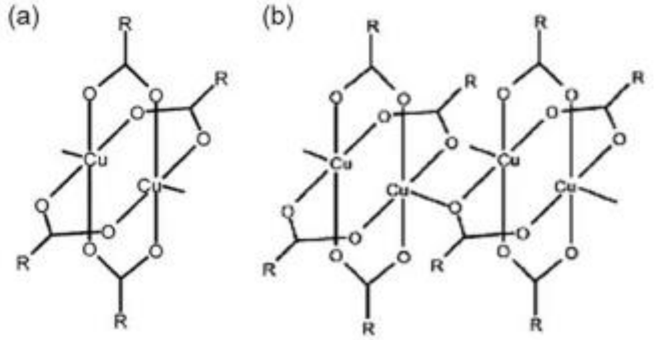

Figure 1The examples of copper(II) carboxylate compounds structures a) a "paddle wheel" dimer b) a polymeric chain.

The studies was focused on the copper(II) and silver(I) compounds, which represent medium and soft metal centers (HSAB theory), respectively. In the case of the [$Ag(O_2CR)$] compounds, the fluorinated and non-fluorinated carboxylate ligands were applied. The carbon chain length and bulky were varied. The secondary ligand influence was studied basing the [$Cu_2(R'NH_2)_2(\mu\text{-}O_2CC_2F_5)_4$] complexes, where R'= Et, ^{s}Bu, ^{t}Bu. The usefulness of a thermal analysis, EI MS spectrometry, and VT IR spectroscopy for the FEBID precursors selection was evaluated.

Acknowledgements: Precursors studies were supported by Nicolaus Copernicus University in Toruń (Statute Research no.103).

References

[1] I. Utke and A. Gölzhäuser, *Angewandte Chemie Int. Ed.,* **49** (2010) 9328–9330.

[2] A. Grodzicki, I. Łakomska, P. Piszczek, P. I. Szymańska, E. Szłyk, *Coord. Chem. Rev.,* **249** (2005) 2232–2258.

[3] I.B. Szymańska,, *Polyhedron*, **65** (**2013**) 82-88.

T-06: Gas assisted focused electron beam induced deposition with low volatility precursors

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The quest for novel precursors suiting focused electron beam induced deposition (FEBID) is ongoing. Driving forces include the FEBID portfolio enlargement of metal elements as well as the objective to obtain directly high metal contents from the non-thermal electron induced dissociation of the precursor adsorbates.

Potentially suitable gas phase precursors for FEBID may have too low vapour pressure at room temperature, mostly due to their small ligands or strong bonds with the metal atom. On the other side small (and few) precursor ligands tend to improve the deposit metal content by nature as not many ligand elements can be co-deposited by the electron induced dissociation. Evidently, to bring such precursors into the vapour phase heating of the gas injection system is needed to temperatures defined by the thermal dependence of the vapour pressure.

To test a precursor compound's sensitivity with regard to electrons, the pristine powder can be directly irradiated in a scanning electron microscope (SEM) and the metal content monitored by energy dispersive X-ray spectrometry [1-3]. When an interesting compound was identified, finding the optimum temperature windows is the next challenging experimental task as often thermodynamic data of the vapour pressure vs. temperature is missing.

In this contribution we describe the general upper and lower temperature limits which need to be respected for gas assisted FEBID. For the precursor reservoir (and gas injection system) the temperature for sufficient molecule flow needs to be established. Surprises can appear when a compound does not congruently evaporate at temperatures assuring practical flow rates but thermally decomposes by losing its ligands. The temperature window on the substrate is given by uncontrolled molecule condensation as lower temperature bound and thermal dissociation, i.e. non-selective chemical vapour deposition (CVD), as upper temperature bound. Although CVD temperatures are often known, the thermal dissociation temperatures were often observed to be lower when working in high vacuum SEM chambers. As well, reversible adsorption/desorption issues were encountered. The talk will be concluded by short examples of precursors investigated during the course of various short term scientific missions with CELINA members.

References

[1] W. van Dorp et al., *Langmuir*, **30(40)** (2014) 12097-105, DOI: 10.1021/la502618t.
[2] J. Warneke et al., *J. Phys. Chem. C*, **120** (2016), 4112−4120, DOI:10.1021/acs.jpcc.5b12184.
[3] K. Hoeflich et al., *ACS Appl. Mater. Interfaces*. **9(28)** (2017), 24071-77, DOI: 10.1021/acsami.7b04353.

T-07: Perfluorinated silver(I) carboxylate compounds for focused electron beam induced deposition (FEBID)

K. Madajska[1], L. Berger[2], M. Polyakov[2], I. Szymańska[1] and I. Utke[2]

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[2] Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, 3602 Thun, Switzerland

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Focused electron beam induced deposition (FEBID) is a direct maskless nanolithography technique, based on the local dissociation of adsorbates upon the irradiation with electrons. It can be used for gas sensors, magnetic sensors, strain sensors, thermal sensors, photodetectors, ferromagnetic wires, superconducting wires, and plasmonic structure deposition [1].

Here we report on our study of three silver carboxylate complexes: $[Ag(O_2CC_2F_5)]$ (1), $[Ag(O_2CC_4F_9)]$ (2) and $[Ag(O_2CCHEt_2)]$ (3) as FEBID precursors. Their use as precursors depends on their ability to be evaporated as intact molecule. Temperature variable infrared spectra analysis for the $[Ag(O_2CC_2F_5)]$ compound indicates the presence of coordinated carboxylate ligands in the gas phase at 413 K, meaning that it can be evaporated congruently [2]. Electron-induced mass spectrometry (EI MS) of the compound $[Ag(O_2CC_2F_5)]$ (1) showing the $[Ag_2(O_2CC_2F_5)]^+$ fragment, the dimeric form $[Ag_2(O_2CC_2F_5)_2]$ was proposed as the main volatile product of the thermal evaporation [3].

SEM observations and EDX measurements of the pristine compound powders (1) - (3) indicated that all three compounds were sensitive to electron beam irradiation as they changed shape or composition when zooming into individual powder grains or fibers. FEBID experiments performed at elevated gas injection and substrate temperatures in Figure 2 showed best results for the precursor (1) with 69-73 at.% silver. This is comparable to 73 at.% silver obtained by earlier FEBID experiments with silver 2,2-dimethylbutyrate as a precursor medium [4]. Precursor (2) gave a silver content of about 9 at.% in deposits, while precursor (3) did not result in silver containing deposits.

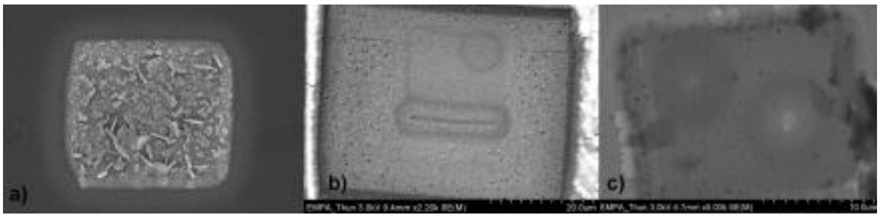

Figure 2: Top view SEM images of FEBID deposits obtained at 20 keV and 0.9 nA on native oxide silicon substrates. a) 10 µm x 10 µm rectangle by $[Ag(O_2CC_2F_5)]$ *(1) showing silver platelets. b) line and dot deposit by* $[Ag(O_2CC_4F_9)]$ *(2), note the halo around these structures, c) dot deposits by* $[Ag(O_2CCHEt_2)]$ *(3) containing no silver.*

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T-08: New FEBID copper precursor under high vacuum for the study of chemical processes induced by low energy electron irradiation

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A study on new class of solid copper precursors for FEBID is presented, more particularly the probing some surface processes involved in the precursor fragmentation under vacuum and by electron irradiation. Complexes of Copper(II) with amines and perfluorinated carboxylates ligands, synthetized in Toruń, Poland, are stable at ambient conditions and are easy to handle.[1] They are directly deposited on silicon and gold surfaces in air and then introduced in vacuum for the study of electron induced fragmentation with surface science tools. This approach is similar to previous studies of different precursors deposited on surfaces and irradiated by 500 eV electrons. [2]

The UHV experimental setup at the ISMO, Orsay, France, is dedicated to the study of chemical processes induced by electron irradiation in supported molecular thin films.[3] It houses two complementary techniques: a High Resolution Electron Energy Loss Spectroscopy Spectrometer (HREELS) and an Electron Stimulated Desorption (ESD) of neutral fragments relying on mass analysis of the fragments using a quadrupole mass spectrometer (QMS). Infrared spectroscopy and (HREELS) show that the precursor is able to spontaneously lose amine ligands under vacuum. This loss can be enhanced by mild heating. The combination of mass spectrometry and low energy electron irradiation (0-15 eV) allows the analysis of neutral fragments released during irradiation. Full amine ligands can be released under irradiation, and perfluorinated ligands are fragmented by electron of energy as low as 1.5 eV. Finally, the cross-section for this process is estimated from temporal evolution in ESD experiments.[4]

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T-09: Synthesis of heteroleptic and -metallic precursors for focused electron beam induced deposition

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Homometallic carbonyls are widely used precursors for nanomaterial synthesis in gas phase processes and in liquids to form metallic coatings or nanostructures. Many of these carbonyls are commercially available and therefore they have been extensively studied. In particular, the deposition of metallic nanostructures by focused electron beam deposition (FEBID) using these homometallic carbonyls has been investigated and optimized in the recent past.[1, 2] In order to circumvent the use of multiple gas sources for the deposition of bimetallic nanostructures hetero-metallic carbonyls have been prepared.

As a proof of concept, $HFeCo_3(CO)_{12}$, $DFeCo_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ have been prepared and structurally compared.[3, 4] The heterometallic carbonyl clusters exhibit low vapor pressure; however, the compounds are volatile enough for the use in FEBID experiments. Despite the similarities in the cluster cores and also in the calculated energy levels, FEBID deposits differ significantly. $HFeCo_3(CO)_{12}$ results in deposits with high metal content (> 80%) while the deposited material using $H_2FeRu_3(CO)_{13}$ contains significantly lower metal content. Structural and chemical similarities as well as differences can help to understand the decomposition behaviour of these molecular precursors.[5]

In order to extend this approach of predefinition of deposit composition via precursor species, a compound containing metal and metalloid has been prepared. The $Mn(CO)_5(SiH_3)$ precursor has been prepared by modified synthesis procedures but similar intermediates described in literature. In contrast to the termetallic precursors described *vide supra*, this precursor is highly volatile at room temperature due to low molecular mass and very limited intramolecular interactions. First results on deposit formation in the FEBIP process and deposit characterisation will be discussed.

This work was conducted within the framework of the COST Action CM1301 (CELINA).

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T-10: Electron induced fragmentation of bimetallic focused electron beam induced deposition precursors.

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Deposition of alloy or composite materials containing more than one metal is a challenge in focused electron beam induced deposition (FEBID). The stakes are high, as such composition control is the key to fabrication of functional nanostructure with well-defined, controllable magnetic properties. Until recently, the deposition of mixed metal structures was realized by using multiple injection systems [1,2]. However, the composition control and reproducibility with this approach has been poor. Recently, an alternative strategy based on the use of a bimetallic precursor, $HFeCo_3(CO)_{12}$, has been demonstrated as a promising approach to produce well-defined mixed metal structures. With this precursor, reproducible direct-writing of nanoscale deposits with high resolution, stoichiometric metal ratio and high metal content (>80 at%) has been achieved [3].

Conversely, the apparently similar bimetallic precursor $H_2FeRu_3(CO)_{13}$ does not hold up to the expectations hatched with regards to the potential of such heteronuclear carbonyls for controlled deposition of alloy nanostructures [4]. In fact, deposits created in FEBID with $H_2FeRu_3(CO)_{13}$ do not exceed a metal content of 26%, the metal content is generally not reproducible and EDX studies indicate proportional iron loss in the deposition process.

Initially motivated by the exceptional performance of $HFeCo_3(CO)_{12}$ in FEBID and the notion of the role of low-energy electrons (LEEs) in the deposition process (see ref. [5] and refs. therein), and later by the very different behaviour of $H_2FeRu_3(CO)_{13}$, we have conducted comprehensive experimental and theoretical studies on LEE interaction with these molecules in the gas phase [3,6,7].

More recently we have extended these studies to the bimetallic heteroleptic $CpFe(CO)_2Mn(CO)_5$ [8], specifically synthesized alloy deposition through FEBID. The combination of the polyhapto cyclopentadienyl group, which is known to be a poor leaving group (ref. 4 and refs therein), and the more labile CO ligands offers an opportunity to compare these ligands in a heteronuclear architecture.

In the current contribution, comprehensive experimental and theoretical studies on the fragmentation of these precursors upon electron attachment and dissociative ionization are presented. The differing performance of $HFeCo_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ is discussed in context to LEE-induced decomposition in the gas phase. The fundamental dissociative electron attachment and dissociative ionization processes observed for these precursors are discussed in relation to their electron-induced fragmentation when adsorbed on surfaces and their performance in FEBID.

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T-11: Complex 3D magnetic nanostructures prepared by FEBID

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Building nanotechnological analogues of naturally occurring magnetic structures has proven to be an extremely powerful approach to studying topics like geometry-induced magnetic frustration and to provide model systems for statistical physics. Moreover, it practically allows to engineer novel physical properties by realizing artificial lattice geometries that are not accessible via natural crystallization or chemical synthesis. This has been accomplished with great success in the field of two-dimensional (2D) artificial spin ice systems over the last decade with important branches also reaching into the field of novel magnetic logic devices, such as, magnetic quantum cellular automata. Although first proposals have been made to advance into three-dimensions (3D), established nano-fabrication pathways based on sophisticated electron beam lithography have not been adapted to obtain free-form 3D nanostructures. Here we demonstrate the direct-write fabrication of freestanding, ferromagnetic 3D nano-architectures, which does, amongst other things, allow for full control over the degree of magnetic frustration. In particular, we have realized free-form shapes featuring three- and four-edge magnetic vertex types as important building blocks for more complex, geometrically frustrated 3D vertex configurations. By employing micro-Hall sensing based on a two-dimensional electron gas, we have determined the magnetic stray field generated by our free-form structures in an externally applied magnetic field. Taking information from microstructure analysis into account, we have performed micromagnetic and macro-spin simulations that allow us to deduce the spatial magnetization profiles in the structures and analyze their switching behavior based on the single-domain magnetic element paradigm followed in 2D artificial spin ice structures. In geometrically frustrated systems, the occurring magnetic configurations as well as the transitions between them are controlled by both, the topology and geometry of the interacting magnetic elements. Our approach allows for the fabrication and magnetic characterization of arrays of free-form 3D structures. Furthermore, the 3D elements made of magnetic material can be combined with other 3D elements of different chemical composition and intrinsic material properties, such as superconducting, plasmon-active, or dielectric materials. We therefore expect that the direct-write approach presented here will inspire innovative free-form design-oriented ideas to engineer nanoscale systems with new emergent physics.

T-12: Electron induced surface reaction of bimetal FEBID precursor molecules $HFeCo_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$

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$HFeCo_3(CO)_{12}$ [1] and $H_2FeRu_3(CO)_{13}$ [2] are precursor molecules used in FEBID to fabricate FeCo and FeRu bimetallic nanostructures, respectively. To date, bimetallic nanostructures have been fabricated in FEBID by mixing two different metal precursor molecules using dual or multichannel precursor gas injection system [3]. However, this approach has limitations to get a good control over the deposit and reproducibility is poor. The use of precursor molecules like $HFeCo_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ in FEBID may offer a rout to eliminate these difficulties.

In fact, nanostructures fabricated with $HFeCo_3(CO)_{12}$ in FEBID have metal content of >80% [1], with excellent reproducibility. In contrast, nanostructures fabricated using $H_2FeRu_3(CO)_{13}$ in FEBID show metal content of only <26% [2]. The different behavior of $HFeCo_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ in FEBID motivated us to study the bond breaking reaction of these precursor molecules adsorbed on a surface, using UHV surface science approach based on X-ray photoelectron spectroscopy (XPS) and mass spectrometry (MS).

From the XPS and MS data, we observed that the initial electron induced surface reactions of $HFeCo_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ are similar, creating a partially decarbonylated intermediate of the form $HFeCo_3(CO)_x$ (x_{avg}~3) and $H_2FeRu_3(CO)_x$ (x_{avg}~4,5), respectively. During typical FEBID experiment, the partially decarbonylated intermediate will experience the effect of either additional electron exposure or transformations initiated by thermal instability. With further electron irradiation, XPS data shows that the CO ligands remained in the $HFeCo_3(CO)_3$ intermediate decompose into C and O but the CO ligands in the $HFeCo_3(CO)_3$ intermediate are thermally unstable at room temperature and desorb almost completely. Consequently, deposits created in FEBD from this precursor will experience the following sequence of elementary reaction steps:

$HFeCo_3(CO)_{12}(ads) + e^- \rightarrow HFeCo_3(CO)_3(s) + 9CO(g)$, $FeCo_3(CO)_3(s) + \Delta \rightarrow FeCo_3(s) + 3CO(g)$

In contrast, additional electron exposure or annealing of the $H_2FeRu_3(CO)_x$ (x_{avg}~4,5) intermediates do not lead to significant CO desorption or CO decomposition. FEBID structures created from this precursor will therefore experience the following sequence of elementary reaction steps:

$H_2FeRu_3(CO)_{13}(ads) + e^- \rightarrow H_2FeRu_3(CO)_x(x \sim 4{,}5)(s) + 8.5\ CO(g)$,

$H_2FeRu_3(CO)_x(x \sim 4{,}5)(s) + e^-/\Delta \rightarrow$ most CO ligands are retained

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T-13: Neutral dissociation: review of experimental approaches

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Since the first meeting of the CELINA cost action, the need for quantitative data (cross sections) on the electron-induced neutral dissociation in FEBID precursors has been stressed. In spite of that, among the elementary decomposition processes, this channel is still the least explored one. The reason for this are the experimental difficulties in the detection of neutral fragments.

In my talk I will review the experiments that have been done in the past on the neutral dissociation of gas-phase molecules. Such experiments were usually rationalized by the need to provide data for plasma modelling and have thus focused on atmospheric and plasma-processing gases. I will pay special attention to the detection techniques and their prospective suitability for nanofabrication precursors. For the few targets, where the cross sections exists, I will compare their magnitude with other decomposition processes such as dissociative ionization or dissociative electron attachment.

T-14: Role of Electronic Excitations in FEBID Processes

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Four mechanisms contribute to the electron-driven degradation of the FEBID precursors: dissociative electron attachment (DEA), dissociative ionization (DI), neutral dissociation (ND) and dipolar dissociation (DD). Thorough understanding of these processes, would ideally, lead to a rational design of precursors where the processes yielding the desired deposit properties dominate. Here, the significance of ND process will be reviewed [1].

ND process is mediated by electronically excited states of a precursor, where electronic excitations from bonding to anti-bonding orbitals can result in a ligand loss along the dissociative potential energy surfaces [1]. Quantum mechanical calculations on precursors, describing their electronic structure and the potential energy surfaces for electronically excited states, are, therefore, inevitable part of the ND studies. These calculations, however, present number of challenges that will be addressed in this talk, along with future perspectives that could lead to better understanding of dissociative electronic excitations.

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T-15: Electron induced fluorescence – detection of neutral fragments

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The photon emission from acetylene induced by electron impact was studied using crossed-beams experiment equipped with an electron monochromator and effusive molecular beam. Besides the discrete transitions we have studied the continuum emission from ethynyl radical in detail. For most important transitions in the spectrum we have determined the emission cross sections and the thresholds for dissociative channels.

The collisions of slow electrons with molecules play an important role in many phenomena such as atmospheric processes induced by radiation from space, low temperature plasma, secondary and back scattered electrons in radiation chemistry, FEBID technologies, etc. The electron induced fluorescence spectroscopy is one of the methods that can be used to study interactions of low energy electrons with molecules and provide new data on the excitation, dissociation and ionization processes in atoms and molecules and especially one of a few methods for detection of neutral products. The acetylene, the smallest hydrocarbon molecule with triple bond, is often used in plasma polymerization, it is abundant in space and its fragments are relevant as FEBID precursor ligands [1,2]. From the spectroscopic point of view the acetylene is quite well known molecule but the emission cross section data are incomplete and sometimes contradictory.

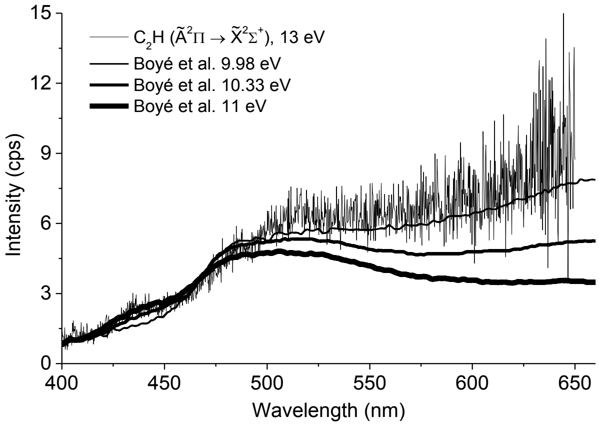

Fig. 1. Ethynyl radical spectrum.

The used experimental device was described in detail in [3]. The apparatus utilizes crossed beams of molecules and mono-chromatic electrons with typical energy resolution of 300-400meV. The system of mirrors and lenses guides the photons emitted during deexcitation to the entrance slit of the Czerny-Turner optical monochromator with thermoelectrically cooled photomultiplier tube working in photon counting regime.

The spectrum was measured in the range from 190nm to 660nm. In the spectrum measured at the 50eV electron energy the lines and bands corresponding to the transitions of C_2H, hydrogen Balmer's series, C_2 and CH were identified. Apart from that we have focused on the emission of the ethynyl radical. Most of the detected lines in the spectrum are superimposed on this continual emission. In the figure 1 the comparison of the ethynyl emission spectrum measured at the electron energy 13eV with the data from [1] is shown. Such energy is below the threshold for other detected excitation processes therefore only the continual radiation is present. The cross sections for ethynyl emission as well as for some of other detected processes were determined in the electron energy range from 5eV up to 70eV.

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T-16: Role of electron self-scavenging in aggregates of $Cr(CO)_6$

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This work is focused on the behavior of $Cr(CO)_6$ aggregates upon interaction with low energy electrons (0 – 15 eV) examined using crossed-beam methods. Strong influence of the environment on the precursor reactivity was observed when compared to the investigation of this molecule in gas phase. [1,2] Similar effect was observed in recently published $Fe(CO)_5$ study [3,4], however unique carbonyl group loss patterns were observed in $Cr(CO)_6$ investigation.

This study was performed using two mass spectrometric setups, first of which allowed high resolution electron energy measurement of resonant electron capture by gas phase molecule, while the second apparatus was used for observation of dissociative electron attachment (DEA) to aggregates of $Cr(CO)_6$. DEA to aggregates of $Cr(CO)_6$ was performed in several regimes regarding clustering conditions, such as pressure and type of the expansion gas, as well as the technique of precursor cluster formation: via co-expansion with rare gases and by pickup of $Cr(CO)_6$ with previously formed argon clusters. This allowed us to probe various sizes of pristine $Cr(CO)_6$ clusters by low energy electron impact, but also to investigate the influence of different matrices on reactivity of the molecule by observing the shift of the resonance positions depending on the clustering conditions. Dominance of low energy resonances observed in gas phase, as well as in the experiment involving the production of small aggregates, was replaced by higher energy resonances (>5 eV) upon the electron impact to larger clusters. This observation is in line with the hypothesis that larger clusters are efficiently shielding the long-range interaction of low energy electrons with their molecular constituents and thus preventing the DEA at energies lower than 5 eV. Further, rather peculiar fragmentation patterns of small $Cr(CO)_6$ aggregates were observed in presence of water in the expansion gas mixture. Formation of negative ions consisting of several water molecules and fragmented $Cr(CO)_6$ molecule, in form $[m(H_2O) \times Cr(CO)_n]^-$ where m = 3, 6, 9 and n = 2, 3, 4, 5, were observed.

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T-17: Nano-fabrication with the Helium Ion Microscope

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Helium Ion Microscopy (HIM) [1,2] is best known for its high resolution imaging capabilities of both conductive as well as insulating samples. However, since the introduction of Ne as an imaging gas for the gas field ion source (GFIS) an increasing number of nano-fabrication applications are realized. While the use of Neon as an imaging gas results in a somewhat lower lateral resolution (1.8 nm for 25 keV Ne compared to 0.5 nm for 30 keV He) the user usually benefits from the much higher cross section for nuclear stopping. The latter results in a larger number of sputtered atoms and bonds broken directly by small impact parameter collisions.

Here, I first want to summarize results obtained over the last years using focused ion beam induced deposition (FIBID) using the HIM [3]. In addition I will show results on resist writing using the HIM. Both approaches benefit from the negligible proximity effect in the HIM. This is related to the different energy distribution of the electrons created by the ion beam as well as the near absence of second or higher generation electrons. Consequently, line patterns with a half pitch of 4 nm have been reported [4]. For high aspect pillars this often results in narrow structures created using FIBID as compared to FEBID.

In the second part I will present results obtained using direct write milling low fluence ion beam irradiation and ion beam based mixing. In all three cases the electronic or magnetic properties of the target material will be altered at the nano-scale in a controlled way to achieve new functionality. The examples comprise

- The fabrication of semiconducting graphene nano-ribbons by direct milling [5]
- The fabrication of a lateral spin valve structure using low fluence ion irradiation [6]
- The formation of individual 3 nm Si clusters for a room temperature single electron transistor

For all presented examples the critical length scale of the nanostructure is smaller or in the range of collision cascade. This size regime can not be accessed with traditional broad beam based ion irradiation and holds many promises but also challenges that need to be overcome to enable new device concepts and new functional materials on the nano-scale.

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T-18: Mechanism-Based Design of Precursors for FEBID

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Focused electron beam induced deposition (FEBID) can create metal-containing nanostructures by using electrons to induce local decomposition of organometallic precursors. For FEBID to emerge as a broadly applicable nanofabrication technique, however, control must be exerted over not just the size and shape, but also the chemical composition of the nanostructures. The common practice has been to use precursors designed for thermal processes, such as chemical vapor deposition (CVD). Unfortunately, organometallic precursors that yield pure metal deposits in CVD generally create FEBID deposits with high levels of organic contamination. We are using mechanistic insights from surface science and gas phase electron-molecule interactions to design organometallic precursors specifically for FEBID [1]. Synthesis of the candidate precursor complexes and evaluation of their electron-induced reactivity under UHV and steady state deposition conditions allow us to identify privileged ligands for use in FEBID. Examples to be discussed include (η^3-C_3H_5)Ru(CO)$_3$X [2, 3], *cis*-Pt(CO)$_2$X$_2$ [4], and CF_3AuCNR where X = halide and R = alkyl.

In related work on gold precursors, trends in volatility with changes in the halide ligand were established for complexes of the type L-Au-X [X = Cl, Br, I; L = PMe$_3$, CNMe, CN^{t}Bu, P(OCH$_2$CF$_3$)$_3$, P(NMe$_2$)$_3$] by determining their sublimation temperatures at a fixed pressure [5]. Within each series L-Au-X, the sublimation temperature T_{sub} decreases with increasing atomic radius of the halide, making the iodide complexes the most volatile. This trend has implications for use of these complexes in FEBID and CVD, for which precursor volatility is critical.

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T-19: An overview of in-situ and ex-situ purification strategies for FEBID gold nanostructures

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Focused Electron Beam Induced Deposition (FEBID) is a direct-write nanofabrication technique where metals can be deposited in-situ in single process step. A gas injection system (GIS) is used to insert the precursor molecule inside the chamber. Among various FEBID materials, gold has received attention due to its applications in plasmonics. FEBID gold has already been utilized to fabricate MOS Capacitors and plasmonics based devices. However low metal content on the deposits hampers the performance of the fabricated structures. This work will give an overview of various in-situ and ex-situ purification approaches which can increase the metal content of noble metal nanostructures.

In the first step, system chamber was cleaned utilizing high-energetic UV light with highly reactive ozone [1]. This cleaning process reduced carbon contamination from residual gas. In second step, Gold structures were deposited with an acceleration voltage 3kV. The structures were exposed to electron beam in presence of different oxidative gases. The chemical composition of the structures were measured using Energy dispersive spectroscopy (EDX).

A specially enhanced process to deposit highly pure gold structures will be shown [2]. In this process, water will be injected as second gas during the deposition in order to perform *in-situ* purification at the same step. In order to investigate the atomic composition, transmission electron microscopy EDX as well as electron energy loss spectroscopy (EELS) will be discussed. In addition, the resistivity of the deposits measured with I-V characteristics will be shown. A theoretical model based on the atomic composition which can explain the high gold content will be presented. In the last step, the applications of the structures purified using various approaches will be discussed. The localized surface plasmon resonance (LSPR) of the structures will be examined by photothermal nanomechanical analysis [3].

In summary, this work will present the investigations on different purification strategies and their applications in nanoelectronic devices.

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T-20: Organic ice resists

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Electron-beam lithography (EBL) is the backbone technology for patterning nanostructures and manufacturing nanodevices. It involves complex synthetic resins processing and handling steps, which are all critical and require dedicated instrumentation and cleanroom environment. Here, we show that simple organic molecules, e.g. alcohols, condensed to form thin-films at low temperature demonstrate resist-like capabilities for EBL applications and beyond. The entire process takes place in a single instrument, and avoids exposing chemicals to the user and the need of cleanrooms. Unlike EBL that requires large samples with optically flat surfaces, we patterned on fragile membranes only 5-nm-thin, and 2 x 2 mm^2 diamond samples. We created patterns on the nm to sub-mm scale, as well as three-dimensional structures by stacking layers of frozen organic molecules. Finally, using plasma etching, the organic ice resist (OIR) patterns are used to structure the underlying material, and thus enable nanodevice fabrication.

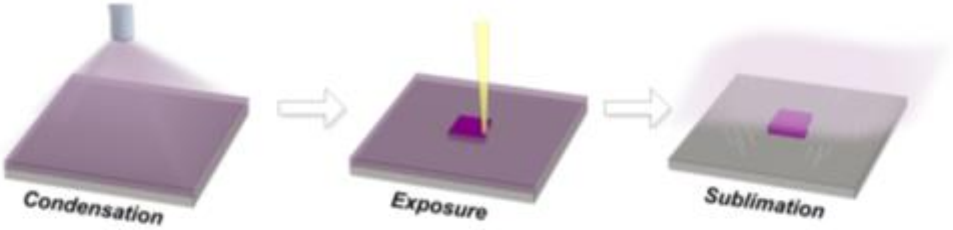

Figure 1. OIR process: a vapour of an organic compound is first condensed onto the cooled sample to form a uniform layer. Its interaction with the e-beam locally modifies its chemical composition resulting in a non-volatile product. When the sample is heated to room temperature the unexposed OIR sublimates while the exposed patterns are stable, enabling ambient downstream processing.

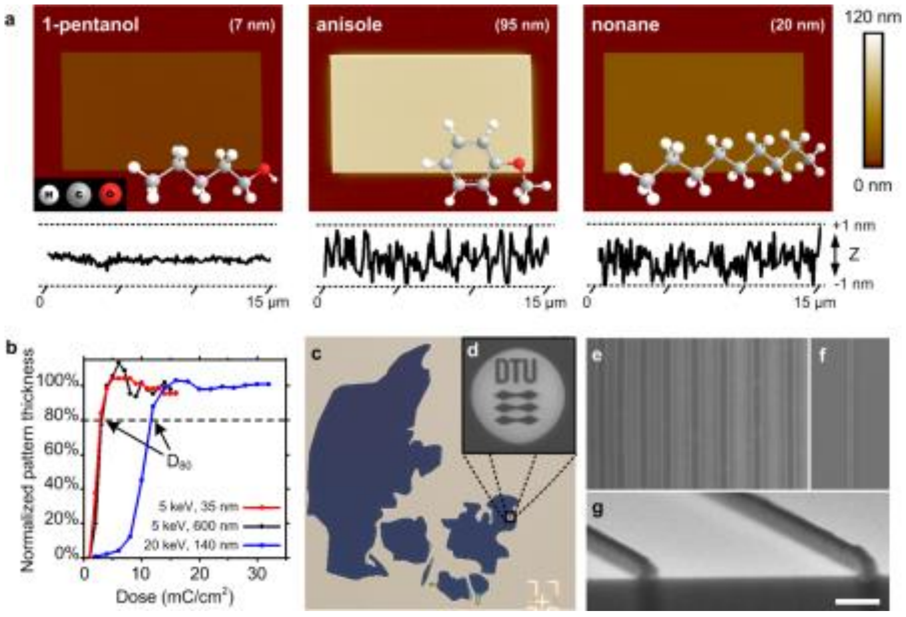

Figure 2. AFM images of 20 x 12 µm^2 rectangles patterned in OIR thin-films and representative scan-lines across the rectangle surface (**a**). **b**, contrast curves for nonane ice at 5 and 20 keV. The critical dose at 5 keV is unchanged even with a 20-fold time increase in thickness. **c-d**, large area map of Denmark made by exposed nonane ice (dark blue areas). The total exposure time was 75 min. The optical image (**c**) covers an area of 0.4 x 0.5 mm^2. **e**, SEM image of 100-nm-wide lines patterned in nonane ice. **f**, 60-nm-wide line patterned in anisole ice. **g**, Tilted SEM view of patterned OIR lines reaching the edge of a 1 x 1 cm^2 chip. The OIR layer is uniform on the entire sample surface, up to the very edge. Scale bar is 200 nm.

T-21: Expanding and Understanding Water-Assisted Purification Procedures: A Case Study of the Potential FEBID Precursor $(EtCp)_2Ru$

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Water-assisted purification procedures for FEBID deposits have recently attracted remarkable attention because they can yield high-purity nanostructures and can easily be conducted in Environmental Scanning Electron Microscopes (ESEMs). Recently, carbonaceous Pt deposits produced from $MeCpPtMe_3$ were purified in the presence of water vapor under prolonged electron exposure in an ESEM leading to pore-free, stable and pure metallic deposits [1]. Similarly, simultaneous dosing of $Me_2Au(tfac)$ and water in FEBID leads to deposits with high Au content [2]. The fundamental chemistry of this process was studied using a surface scientific model approach with thin deposit layers of defined thickness [3]. Herein, we present a study on a potential FEBID precursor containing the less noble central metal Ru, namely, bis(ethylcyclopentadienyl)ruthenium(II) ($(EtCp)_2Ru$, Fig. 1) which aims at revealing whether water-assisted purification approaches are applicable for a wider range of metals.

$(EtCp)_2Ru$ has been considered as precursor for FEBID due to the potential use of Ru for Extreme Ultraviolet (EUV) lithography mask repair [4]. An oxygen-based purification procedure was used to reduce the initial carbon content in the as-deposited state (Ru:C 1:9). Here, we report evidence for a successful water-assisted purification to Ru deposits. Oxidation of the less noble Ru does occur but a proper set of purification parameters in the ESEM might yield high-purity Ru deposits. Further improvement of the parameter set is indeed needed to maintain stable shapes throughout all deposit processing steps. Complementary surface studies on thin deposit layers of $(EtCp)_2Ru$ employing mass spectrometry reveal volatile products released during both deposition and water-assisted purification processes under a broad electron beam. These results give insights in the fundamental chemistry involved in the production and purification of FEBID based nanostructures made from $(EtCp)_2Ru$.

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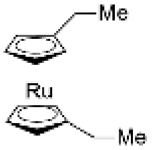

Figure 3. Molecular formula of bis(ethylcyclopentadienyl)ruthenium(II) $(EtCp)_2Ru$.

T-22: Direct Electron Beam Writing of Silver-Based Nanostructures

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The direct writing using a focused electron beam (FEBID) for the local decomposition of a precursor medium is a process which allows for the fabrication of truly three-dimensional structures on the nanometer scale [1]. One important challenge, however, is the identification of appropriate precursors which allow for a deposition of the material of choice in combination with the full 3D capabilities [2] e.g. for envisaged applications in nano-optics [3]. In this respect the coinage metal silver is of particular interest since it shows a relatively high plasma frequency, and thus, excellent plasmonic properties in the visible range [4]. However, silver FEBID is not trivial as the low vapor pressures of typical precursor candidates necessitates heating of the precursor reservoir to achieve reasonable gas supply as well as heating of the substrate to avoid condensation. Simultaneously thermal dissociation needs to be prevented.

By utilizing the precursor compound AgO_2Me_2Bu, direct writing of silver-based nanostructures via local electron beam induced deposition could be realized for the first time [5]. Interestingly, the silver deposition was strongly dependent on electron dose; at low doses of 30 nC/ µm2 a dominant formation of pure silver crystals was observed, while at higher electron doses around 104 nC/µm2 large carbon contents were measured. A scheme for the enhanced silver deposition under low electron fluxes by an electronic activation of precursor dissociation below thermal CVD temperature is proposed and validated using material characterization techniques. Finally, the knowledge gained was employed to fabricate well-defined two-dimensional deposits with maximized silver content approaching 75 at. %, which was achieved by proper adjustment of the deposition parameters. The corresponding deposits consist of plasmonically active silver crystallites and demonstrate a pronounced Raman signal enhancement of the carbonaceous matrix.

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T-23: Low energy electron triggered fragmentation of metal acetylacetonates

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Focused Electron Beam Induced Deposition (FEBID) is one of the most attractive methodology that allows a direct-writing with nanometer resolution [1,2]. This technique consists of the deposition of a material onto a substrate which is then subjected to a highly focused, high-energy electron beam. The degradation of the precursor molecules occurs via various decomposition processes such as neutral dissociation, dissociative ionization, dipolar dissociation, and dissociative electron attachment (DEA) [3]. For the DEA processes, which involve electrons typically with energies below the ionization threshold of the molecule (≈ 8-10 eV), the molecular dissociation occurs, in general, with a relatively high cross section [4].

Organometallic complexes, originally designed for chemical vapour deposition (CVD) purposes, have been recognized as promising FEBID precursors. In the present contribution we report the results from dissociative electron attachment to gas phase transition metal acetylacetonates in the energy range of 0 – 12 eV. In particular, we study the electron attachment to copper(II) acetylacetonate, cobalt(II) acetylacetonate, and manganese(II) acetylacetonate. The DEA to Metal(acac)$_2$ results in the formation of various species among which the most intense are those attributed to the formation of the [Metal(acac)$_2$]$^-$ and [acac]$^-$ anions. Both of these anions are generated in the low energy range. Surprising, their relative intensities differ substantially when going from the lower group to the higher one. This effect will be discussed during the presentation.

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T-24: Instrumentation for neutral radical detection from gas-phase molecular dissociative electron attachment

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Electron attachment to a molecule triggers several dissociation pathways of transient molecular anions, each resulting in the formation of one negative ion and its counterpart. The counterpart can be a single neutral radical or several fragments. However, there are no studies that detect the neutrals formed from the dissociative electron attachment (DEA) process to molecules in the gas phase. In order to do this, we developed stepwise electron spectroscopy (SWES) [1]. We detected the neutrals produced upon DEA to CCl_4 at ~0 eV by measuring the appearance energies of CCl_3 radical as well as the other neutral species. In addition, we combined the experimental findings with high-level quantum chemical calculations to obtain a complete analysis of both the DEA to CCl_4 and the subsequent electron-impact ionization of CCl_3 radicals.

The detection of neutral radicals can be essential from the point of view of development of industrial applications, such as high-resolution nanolithography [2,3]. Radicals can be essential in chemistry involved in electron induced nano-fabrication, but it is still undetermined what types of neutrals are produced from DEA and their role in material growth. Thus, the detection of neutral radical can advance our understanding of the molecular mechanisms accompanied nanofabrication.

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T-25: FEBID of W and Pt precursors at very low energy

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FEBID is typically performed at medium-high energies (5-30 keV) to achieve the best spatial resolution in nanolithography applications. The dissociation cross-section of gas precursor molecules, however, is peaked at much lower energies (few tens of eV), causing low deposition yield and low purity of the deposit due to incomplete molecule decomposition during the process.
The aim of this short scientific mission was to study the deposition of two common metal precursors ($W(CO)_6$ and $MeCpPtMe_3$) down to very low electron energy (20 eV), using a state-of-the-art FEBID apparatus (FEI Helios 650 Dual Beam), capable of achieving low electron landing energies without compromising beam resolution. Depositions were performed in a broad energy range (20 eV - 5 keV) and analyzed by SEM imaging, EDX spectroscopy and atomic force microscopy (AFM).

- $MeCpPtMe_3$ FEBID was performed on a FIB-cleaned Si substrate with a new gas injection system (GIS), under patent consideration, designed to minimize the retarding field distortion induced by GIS insertion. 1 μm-squares were deposited in the 40 eV - 5 keV energy range. Deposition yield distribution measured by AFM (Fig.1) is quite broad and peaked around 200 eV. Composition on the thicker samples gives 35 at.% of Pt and 65 at.% of C. Deposit shape is flat-top like (Fig.1), indicating an electron-limited regime.
- $W(CO)_6$ FEBID was performed on a GaAs substrate with a standard GIS, kept in retracted position. 0.5 μm-squares were deposited in the 20 eV - 5 keV energy range. Deposition yield curve measured by AFM is much narrower and peaked around 120 eV (Fig.1). Deposit composition on the thicker samples gives 50 at.% of W and 35 at.% of C and 15 at.% of O. Square deposits show a saddle-shape (Fig.1) typical of a precursor-limited regime as a consequence of the low precursor flux.

Results will be discussed.

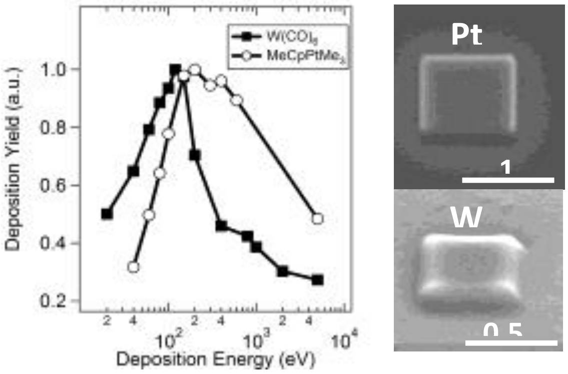

Fig.1 (left) Deposition Yield measured by AFM and (right) SEM images of Pt and W squares deposited at 80 eV.

T-26: Amplified cross-linking efficiency of SAMs through targeted DEA for the production of CNMs

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Carbon Nano Membranes (CNM) are mechanical stable and homogeneous quasi 2D systems which are formed by the electron radiation induced cross linking of molecules in specific self-assembled monolayers (SAM) grown on substrates like e.g. gold or copper. Contrary to graphene, as the most popular 2D system, the CNM structural and functional properties can be tailored by the selection and composition of appropriate precursors for the SAM formation as for instance phenylthiols or naphthalenes [1,2].

The determination of the negative ion yields of 2'-chloro-1,1'-biphenyl (2-Cl-BP), 2'-bromo- 1,1'-biphenyl (2-Br-BP) and 2'-iodo-1,1'-biphenyl (2-I-BP) up on dissociative electron attachment (DEA) [3] at electron energies of 0 eV revealed a more than ten times higher cross sections for iodide loss from 2-I-BP than for the loss of the other halogenides from the respective BPs. Inspired by this result, SAMs from equally halogenated biphenylthiols were grown on Au(111) substrates and exposed to 50eV of electron radiation. Dosis dependend XPS measurements were performed in order to study the influence of a higher cross section for the iodide loss on the cross linking efficiency and the formation of CNMs.

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Poster Abstracts

P-01: Combined Electron-Stimulated Desorption and Infrared Spectroscopic Study for FEBID Precursors with Low Volatility

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A precursor for electron beam-induced deposition must meet a number of requirements regarding its properties. On the one hand it should be stable enough to be stored and handled easily and on the other hand it must contain ligands that will readily decomposed under electron irradiation only leading to volatile fragments and a single pure metallic deposit. In addition, the precursor itself must be sufficiently volatile to be introduced to the reaction chamber via gas phase. Due to advancing developments in the field of gas injection systems it is now possible to handle even low volatile precursor compounds that require elevated temperatures to generate sufficiently high vapor pressures. Two examples for such compounds are the well-known anti-cancer drug cisplatin (*cis*-diamminedichloroplatinum(II)) [1] and Ag-(2,2- dimethylbutanoato-κO) [2], a promising precursor for silver deposits. Both compounds show a good sensitivity towards electron beam impact but require special gas inlet systems. For the latter optimal deposition rates were reached at temperatures of 150°C.

To study the decomposition such low-volatile or even pre-deposited FEBID precursors upon electron exposure we recently set up a new UHV chamber for electron stimulated desorption (ESD) experiments. It allows us to insert externally prepared samples into UHV. These samples are either prepared by sublimation in a separate setup or grown from solution onto a conductive substrate In combination with reflection absorption infrared spectroscopy (RAIRS) performed before and after irradiation we are able to study the electron-induced decomposition of the samples in an energy range between 10 and 500 eV. The combination of both techniques enables us to observe both neutral fragments released to the gas phase upon electron exposure and to obtain chemical information about the remaining deposit. ESD and RAIRS data of different precursors are presented to investigate their tendency to release their ligands under electron exposure.

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P-02: The new thin layers of the Ag(I) and Cu(II) Schiff base complexes obtained by the wet methods

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Some of transition metal complexes with various Schiff bases have been used as catalysts, components of organic light emitting diodes (OLED), thin-film organic solar cells or for the preparation of self-assembling layers. Copper(II) and silver(I) complexes of Schiff bases and nitrogen donor ligands are known for their biological role and fluorescence properties.[1-2]

In this work Ag(I) and Cu(II) complexes with Schiff bases were obtained and spectroscopically characterized. X-ray crystal structures of Ag(I) and Cu(II) complexes have been determined. Thin layers of studied silver(I) and copper(II) complexes were deposited on Si(111) substrates by a spin- and dip- coating techniques and characterized by scanning electron microscopy (SEM/EDS) and atomic force microscopy (AFM) (Figure 1). Fluorescence spectra of complexes and obtained layers were studied in the UV-Vis range. The highest fluorescence intensity was noted for the layers obtained by a multistage deposition at different spin rates and deposition time 5 s. Some of the layers were heated under nitrogen atmosphere. The layers of the copper oxide was the final product of thermal decomposition of the layers.

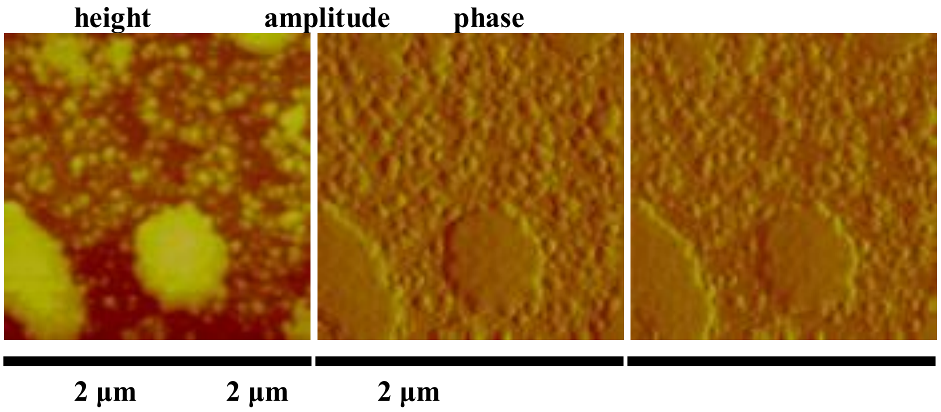

Figure 1. AFM images of [Cu(II)(-)chxn(3,5-^{t}Buba)(5-nba)] (spin coating 100 rpm, 5s), after heating, magn. 2 µm.

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P-03: Gas Assisted Silver Deposition with a Focused Electron Beam

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Focused electron beam induced deposition (FEBID) with silver from the gas phase has not been investigated in great extent so far. Silver represents a highly interesting material for the maskless direct-write fabrication of plasmonic applications [1-3]. In this work we report the suitability of the Ag(I) compound silver(I) pentafluoropropionate ($AgO_2CC_2F_5$) as a FEBID precursor which has been used before for chemical vapor deposition (CVD) [4]. Our results show that FEBID can be conducted at much lower substrate and precursor temperatures than those of 540 K previously reported for CVD experiments, and resulted in selective deposition with high metal purity reaching up to 76 % of Ag (Fig. 1). The results were characterized with SEM, EDX and TEM. HR-TEM images as in Figure 2 a display the crystalline nature of the silver metal deposits which can be obtained by FEBID. The spot deposit was selectively written with an acceleration voltage of 25 keV and 0.25 nA, the shape of which is defined by the size of the primary electron beam (core line) and the range of backscattered electrons (halo deposit) (Fig. 2 b). Different crystal growth is observed in the peripheral area as well as for different precursor refreshment times. Additionally, selected area electron diffraction (SAED), Raman and electrical measurements were conducted to characterize the purity of the silver deposits. We will present our results and discuss further implications for this precursor which appears to be a promising candidate for successful silver FEBID.

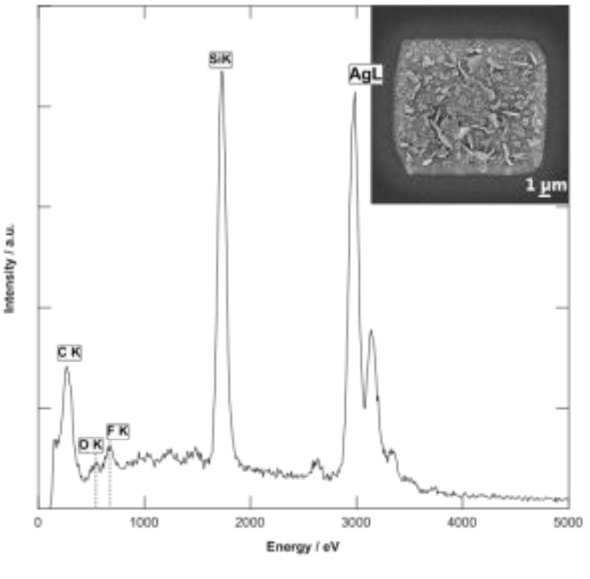

Figure 1 – EDX spectrum of a silver rectangle written by a focused electron beam (20 keV, 0.9 nA) on a native SiO2/Si substrate. The metal content was determined to be 76 % after subtraction of the substrate signal. The inset displays a SEM image of the deposit.

P-04: Quantum Chemical Calculations on the electron-induced formation of formamide from NH_3 and CO

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A profound understanding of the mechanism of a chemical reaction is fundamental for a better control of its outcome. In the case of reactions initiated by electron exposure, intermediates are often difficult to monitor experimentally so that the details of a reaction leading to a specific product often remain speculative. Therefore, quantum-chemical studies of the reaction pathways following the initial electron-molecule interaction are important to arrive at a comprehensive picture. As an example, this contribution presents calculations aiming at rationalizing the electron-induced formation of formamide ($HCONH_2$) in condensed mixtures of NH_3 and CO [1]. While this example relates to research aiming at unravelling reactions that occur under astrochemical conditions, the general approach may also help to understand particular aspects of the electron-induced chemistry inherent in FEBID.

As shown recently by use of thermal desorption spectrometry (TDS), electron exposure of cryogenic condensed mixtures of NH_3 and CO leads to the formation of formamide. This is the smallest possible molecule with a peptide bond and thus can serve as a model compound for organic molecules formed on icy dust particles in space. Its formation as a consequence of electron impact ionization of the parent compounds was anticipated based on the analogous electron-induced synthesis of ethylamine (H_2CCHNH_2) from NH_3 and ethylene (C_2H_4) reported earlier [2]. However, the dependence of the yield of formamide on the electron energy revealed that two different reaction channels must be involved in its formation [1]. We have thus performed quantum chemical calculations at the B3LYP/6-311++G(d,p) level of theory to explore the most likely reaction pathways following both dissociative electron attachment (DEA) at ~9 eV and electron impact ionisation (EI) at > 12 eV. These results help to rationalize the exclusive formation of formamide without possible by-products such as urea or formaldehyde.

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P-05: Electron-driven chemistry of water

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FEBID deposits are often dominated by carbon rather than the metal of interest. Especially the extensive work on $MeCpPt^{IV}Me_3$ has shown that up to 80% by atom numbers of the deposit can be carbon rather than platinum. However, in the case of $MeCpPt^{IV}Me_3$, Geier *et al.* have shown that a treatment of the deposit by electron exposure in the presence of water vapor is an efficient way of reaching high metal purity [1]. The underlying mechanisms of the reactions involving deposit, water and electrons are currently studied by Rohdenburg *et al.* [2].

A look at the literature of electron induced processes in H_2O reveals that on top of various electronically and ro-vibrational excited states, a number of very reactive ionic and radical species can be formed [3]. At high electron energies, as the 5 keV used in the Geier *et al.* study, the primary interaction cross section of electrons with H_2O is not too large and predominantly produces H_2O^+, OH^+ and H^+, as well as a secondary electron. These electrons, with typical energies between near 0 eV and about 20 eV, however, have large cross sections for the production of the extremely active species H^-, O^- and OH^-. Various oxidative processes with remaining CO ligands or carbonaceous deposits are possible.

On top of this well-known chemistry of H_2O under an electron beam, this molecule can enable other reactions as well. Warneke *et al.* showed that the presence of H_2O can stabilize otherwise inaccessible transient negative ions, thus enabling chemical reactions that are not possible in the absence of H_2O [4]. The formation of ethanol (C_2H_5OH) as well as butane (C_4H_{10}) from ethylene (C_2H_4) at energies lower than 3 eV demonstrated this effect. The primary step of the reaction is electron attachment to C_2H_4, yielding $C_2H_4^{\bullet-}$. In the gas phase, this radical anion quickly decays by autodetachment of the electron. The presence of water with its acidic protons however enables the production of the ethyl radical ($C_2H_5^{\bullet}$), which is much more stable than $C_2H_4^{\bullet-}$ and leads to a variety of products at typical secondary electron energies, while in the absence of water, no reactions of C_2H_4 were observed as such low energies [5]. Furthermore, alcoholic species as formed by these reactions tend to fragment via loss of CO under electron exposure [6]. Overall, this opens an effective reaction channel leading to conversion of organic material in a FEBID deposit to volatile species.

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P-06: Vanadyl complexes in catalyzed olefin epoxidation

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The mononuclear oxovanadium(IV) complexes [VO(acac)(R-BIAN)]Cl (BIAN = 1,2-bis{(R-phenyl)imino}acenaphthene, R = H, **1**; CH_3, **2**; Cl, **3**) promote the catalytic oxidation of olefins (cyclohexene, *cis*-cyclooctene, styrene, *S*(−)− and *R*(+)−pinene, *S*(−)− and *R*(+)−limonene) with tbhp (*tert*-butylhydroperoxide) as oxidant. H_2O_2 can be also used in the oxidation of cyclohexene, *cis*-cyclooctene, and styrene, but conversions are lower than with tbhp. The best results were obtained when complex **3** epoxidized styrene with H_2O_2 with a TOF of 290 mol $mol^{-1}{}_V$ h^{-1} and **2** oxidized *cis*-cyclooctene with tbhp reaching a TOF of 248 mol $mol^{-1}{}_V$ h^{-1}. V(V) complexes are considered to be the active species in oxidation reactions of alkenes, though the activity of V(IV) active species has never been totally discarded. With a combination of several techniques (EPR, UV-vis, HRMS, DFT) we could prove the role of V(IV) intermediates in these reactions. We show here the relevance of high-resolution mass spectrometry (HRMS) experiments.

Complex **1** was mixed with tbhp (ratio 1:10) in acetonitrile (under conditions similar to those used in the UV/Vis experiments) in order to search the active catalytic species. Analysis of the resulting mixture (after addition of methanol for a good quality spray) showed the presence of a single vanadium species at m/z = 611.24, which can be formulated as $[C_{33}H_{40}N_2O_6V]^+$ and corresponds to the species $[VO(H{-}BIAN)(tbhp)_2(CH_3OH)]^+$. It easily loses the methanol molecule to yield the complex $[VO(H{-}BIAN)(tbhp)_2]^+$ detected at m/z = 579.21, that may be considered the active species, according to DFT calculations This result shows that, in the presence of tbhp, complex **1** loses easily the acac ligand, which is replaced by two tbhp moleculesUse the *Bulleted* style for a list of bullet points:

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P-07: Electron-Beam Plasma processing of liquid and gas-phase hydrocarbons

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Electron-Beam Plasma processing of liquid and gas-phase hydrocarbons driven by electron-beam is studied experimentally and supported with quantum chemistry calculations. Primary fast electrons are injected in gas medium involving different processes. These electrons release energy to the medium and are continuously decelerated through inelastic collisions. During this process, the primary electron produces secondary electrons and induces dissociative electron attachment, electron attachment, recombination, excitation and formation of radicals in the precursor gas molecules, as well as during experiment with liquids hydrocarbon samples. inducing cleavage of long molecules producing shorter ones. The studies have been carry out inside a plasma-chemical reactor operating at low temperatures. In the work, it is considered that the Electron Energy Distribution Function (EEDF) in electron-beam plasmas is non-Maxwellian. This has promising advantages from the point of view of industrial applications. Analyses of the plasma has been performed using mass spectroscopy, fiber optic spectrometry, CCD Camera imaging as well as electric diagnostics techniques using Langmuir probes. For improved understanding of reaction mechanisms and pathways during the plasma process, quantum chemical calculations were performed as way to study the reactions through which electrons induce the cleavage of molecules and thus the synthesis of new products that were observed during the mass spectrum analysis. The effect of plasma processing over liquid phase processed samples was studied through viscosity measurement. The achieved results suggest that the interaction of fast electrons with gas precursors produces cracking of the molecules with promising potential applications of non-thermal plasma processing of hydrocarbons for environmental, energy, nanomaterial and industrial applications with high efficiency, low energy consumption, high safety and low environmental impact.

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P-08: Controlled electron induced cross-linking of self-assembled monolayers for carbon nano-membrane production and functionalization; project and perspectives.

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Carbon nano-membranes (CNMs) are molecular membranes with thicknesses of 1 to few nm, high thermal stability and mechanical strength [1,2]. In recent years, the Gölzhäuser group at the University of Bielefeld has developed protocols and procedures to produce functional CNMs by electron induced cross-linking of aromatic self-assembled monolayers (SAMs) [2]. The cross-linking is mainly attributed to electron induced C-H bond rupture in the monomers in the SAMs [3]. However, low energy electron induced bond rupture can proceed through distinctly different processes, i.e., dissociative ionization (DI), neutral or dipolar dissociation up on electronic excitation (ND and DD, respectively) or through dissociative electron attachment (DEA)) [4-6].

The current project is based on the notation that controlled cross-linking and functionalization of CNMs can be achieved by taking advantage of the different nature of these processes and in particular the bond selectivity and efficacy of DEA. In fact, first experiments in this direction were recently conducted on the halogenated biphenyls 2-iodo-biphenyls (2-IBP), 2-bromo-byphenyls (2-BrBP) and 2-chloro-byphenyls (2-ClBP), comparing their cross-linking efficiency. Apparently the expect high DEA cross sections at 0 eV for 2-IBP as compared to 2-BrBP and 2-ClBP is reflected in the cross linking efficiency of these compounds supporting the notation that DEA may be used to increase the cross-linking efficiency of SAMs for the production of CNMs.

The project aims to better understand the low energy electron induced chemistry behind the cross-linking of SAMs with the aim to improve the control over the CNMs production and to increase the cross-linking efficiency. Properties of substituted aromatic compounds for the production of CNMs from SAMs through low energy electron induced cross-linking will be characterized in the gas phase within the research group Prof Oddur Ingólfsson in Reykjavík. Model compounds, sensitized towards DEA will be provided by the group of Prof. Terfort group at the Goethe University in Frankfurt. The production of functional Carbon Nanomembranes (CNMs), based on the gained information, will then be carried out within the research group of Prof. Gölzhäuser at the University of Bielefeld.

In the current contribution we present the concept of this approach and discuss previous results in conjunction to the next steps planned within this project.

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P-09: A new copper precursor for EBID

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High electrical and thermal conductivity are the most famous properties of copper and the reason it is commonly used in electric and electronic devices. Together with its high abundance and cheap price copper was one of the most important metals in the 20th century used for cables, generators and transformers. During the last years FIBID and EBID has been used to electrically contact nanometre-sized materials. This depositions were always performed with a platinum containing precursor which is very well investigated, regarding deposition parameters, conductivity and purification methods. Comparing the bulk resistivities of platinum and copper, platinum is about 6 times as high. Making copper the more favorable material for electrical wires. While silver and gold are two of the most prominent materials used for plasmonics, so far only a few investigations about plasmonics with copper have been made. Even though in the periodic table copper stands above silver and gold in the 11th group of the periodic table, featuring the same electron configuration of a full d band and a half filled s band. The similar configuration suggest that the properties of copper could be as well suited for plasmonic applications. The desired configuration for plasmonic applications is a high negative value of the real part of the permittivity and a low value of the imaginary part. Indicating a strong localization of the electro-magnetic field and a low absorption respectively. The copper precursor $Cu(tbaoac)_2$ is investigated by its deposition parameters for nanostructures and planar deposits. Further are its optical properties determined and confirmed by darkfield scattering measurements and simulations.

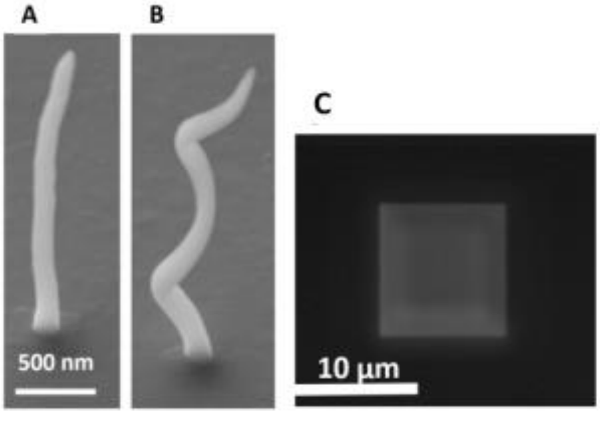

Figure 4 A,B) Scanning electron micrograph of nanostructures fabricated with the new copper precursor. C) Scanning electron micrograph of a square deposit on a transparent substrate used for transmission/reflection measurement to determine the permittivity.

P-10: Comparison of gas silver precursors for FEBID: silver-dimethylbutyrate and silver-butylacetelide

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Focused electron beam induced deposition (FEBID) is one of the most promising methods which can be used for fabrication in the nanometer range. As a maskless and direct method of writing structures it can stand as a real alternative for commonly used many-steps lithographic techniques[1]. One of the most important features of FEBID is the possibility to create truly three dimensional objects[2]. Despite its advantages, there are still only few chemical elements, which were successfully deposited with high purity level[1]. Routes to achieve the highest purity deposits include synthesis of FEBID appropriate precursors, optimization of deposition parameters, and post-growth treatments. Pure metal deposits are crucial for applications in nano-optics [3]. Due to its plasmonic properties in the range of visible electromagnetic waves, metallic silver is a promising material for nanostrucutures used in optics. Identifying proper precursors, which will be both volatile at moderate temperatures and sensitive for the e-beam irradiation, is pre-requisite for successful FEBID experiments. This study presents the comparison between two compounds: silver butylacetelide (AgMe2Bu) and silver dimethylbutyrate (AgO2Me2Bu). Electron beam irradiation and energy dispersive X-ray spectrometry on the solid compounds showed high electron sensitivity for AgO2Me2Bu while AgMe2Bu did not change morphology and composition. FEBID experiments resulted for the first time in silver containing material for AgO2Me2Bu as gaseous precursor[4] while AgMe2Bu FEBID was not successful. A slight dependency of the electron beam dwell time on the silver content and grain size was found. The experimental results were confronted with Monte Carlo simulations of e-beam interaction to develop a preliminary model of FEBID for AgO2Me2Bu.

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P-11: Dissociative electron ionization studies with Chromium Hexacarbonyl Cr(CO)6

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Focused Electron Beam Induced Deposition (FEBID) allows the production of three-dimensional nanoscale structures on surfaces. Briefly, a highly energetic electron beam interacts with metalorganic precursors introduced by a gas injection system leaving a metallic deposit on a surface [1]. The purity-level and spatial resolution of the deposits are major limitations. Secondary electrons such as low-energy electrons (LEEs) are produced from ionizing processes as well as from the interaction of high-energy electrons with the surface. LEEs with energies above the precursor's ionization threshold can trigger, for instance dissociative electron ionization (DEI) reactions leading to a diminution of the deposit quality. Therefore, in order to improve the quality of the metallic deposit it is crucial to achieve a better understanding of electron induced chemistry underlying FEBID.

Chromium containing compounds are used in FEBID as precursor molecules due to the claimed purity of the deposit [2]. We investigated DEI of $Cr(CO)_6$ upon electron ionization at the electron energy of 70 eV as well as the dissociation of metastable cations in the microsecond range [3]. Additionally, we stimulated collision induced dissociation (CID) of the parent cation, $Cr(CO)_6^+$.

The measurements were carried out using a double focusing two sector field mass spectrometer in reversed Nier-Johnson geometry. A collision cell was placed in the second field-free region. Ambient air was used as collision gas.

The recorded mass spectrum agrees with previous studies where the formation of the bare metal cation, Cr^+, was reported to be the most intense fragmentation channel [4,5]. However, in the present study, $Cr(CO)^+$ and Cr^+ represent preferable fragmentation channels. A series of $Cr(CO)_nC^+$ ($0\leq n\leq 3$) cations formed by the cleavage of the C-O triple bond is identified for the first time, in addition to the previously identified series $Cr(CO)_n^+$ ($0\leq n\leq 5$). Doubly charged cations are observed as well. Namely, the series $Cr(CO)_n^{++}$ ($0\leq n\leq 5$) and $CrC(CO)_n^{++}$ ($0\leq n\leq 3$).

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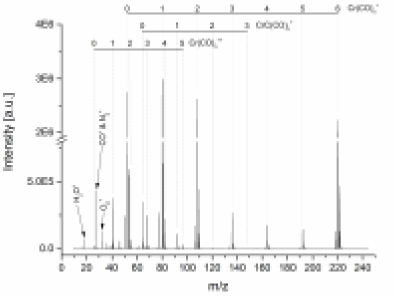

Figure 1. Dissociative electron ionization mass spectrum of $Cr(CO)_6$ obtained at 70 eV electron impact energy

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P-12: Dissociative electron attachment to cyclopentadienylmanganese(I) tricarbonyl

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In the present work a dissociative electron attachment (DEA) to cyclopentadienylmanganese(I) tricarbonyl, $(C_5H_5)Mn(CO)_3$, has been investigated. Molecule can be considered as potential FEBID precursor. This samle has extremely high sublimation rate and adsorb on filament of ion gauge, so measurements were hard to perform. Measurements were done utilizing an experimental setup [1] settled in Siedlce, Poland. Briefly, it consists of trochoidal electron monochromator (TEM), quadrupole mass analyzer (QMA) and secondary electron multiplier, all enclosed into vacuum chamber. Incident electron beam, with energy resolution of FWHM ≈ 160meV, orthogonally crossed with molecular beam resulting in the formation of fragment anions. The obtained mass spectra were recorded for the energies from 0 eV to 8 eV, with 2 eV step. The compound showed weak features, at energy near 0 eV, that are due to the loss of one or two carbonyl groups: $(M - CO)^-$ = 176 a.m.u., $(M - (CO)_2)^-$ = 148 a.m.u. Temperature was around 45°C and the pressure around 4.4×10^{-7} mbars.

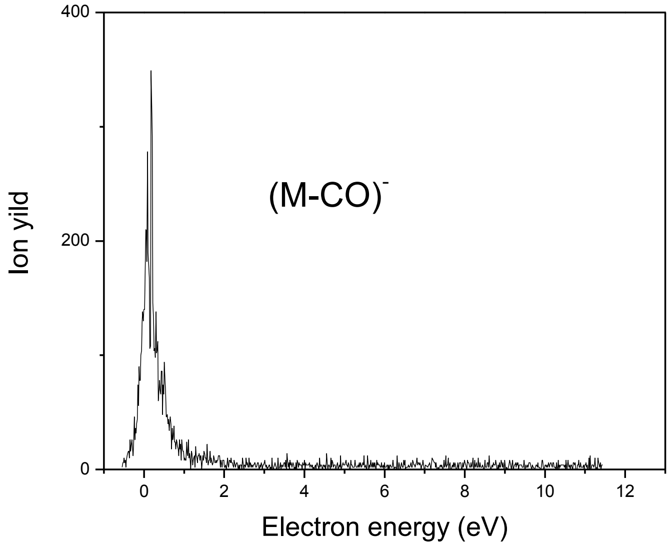

Fig.1. Ion yield of $(M-(CO))^-$, produced from electron impact on gaseous cyclopentadienylmanganese(I) tricarbonyl.

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P-13: Experimental electron scattering total cross sections from tin tetrachloride ($SnCl_4$) molecules

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Strong interest in research on electron-molecule collisions is mainly due to their important role in many field of science and wide range of applicability. At the Conference experimental total cross section (TCS) for electron scattering from tin tetrachloride ($SnCl_4$) molecules will be presented. This data can be useful for modeling plasma reactors and metal halides laser development. $SnCl_4$ is also considered as a potential precursor in nanostructure composition during focused electron beam induced deposition (FEBID).

Results have been obtain with linear electron-transmission method using the electrostatic 127° electron spectrometer for electron energies ranging from 0.6 to 300 eV. Preliminary TCS energy dependence have been shown in fig.1.

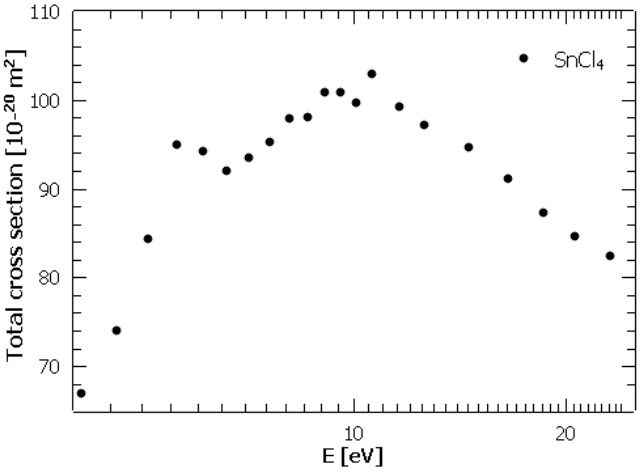

Fig. 1. Preliminary results of experimental TCS for electron scattering from SnCl4.

Detailed discussion of the results and comparison with another molecules with tetrahedral symmetry (CCl_4 [1], $SiCl_4$ [2], $GeCl_4$ [3]), which were studied at the same laboratory with the same experimental method, will be presented during Conference Poster session.

Acknowledgments: This work has been partially supported by the Polish Ministry of Science and Higher Education. Sylwia Stefanowska kindly acknowledge the support of the Polish Ministry of Science and Higher Education within the Diamond Grant program (project no. DI2015 018945).

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P-14: 3D-nanoprinting using Electron Beam Induced Deposition

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The potential of EBID as a 3D-nanoprinting technique has not yet been fully explored. Researchers have mostly taken an experimental approach to determine deposition parameters like dwell time, pitch, and precursor flux. Only recently an attempt was made to create a simulation model to guide the structure fabrication [1]. Inspired by their work we have attempted to reproduce and elaborate on some of these structures to assess whether it is possible to write any arbitrary structure.

All structures were deposited on a Si substrate using the $MeCpPtMe_3$ precursor, in an FEI NovaNanoLab 650 SEM, at 5 keV, 98 pA, and a pressure between $9\cdot10^{-6}$ and $2\cdot10^{-5}$ mbar during deposition. It is assumed that an increasing dwell-time-per-pixel results in an increasing vertical growth-component. We noticed that for taller structures the growth decreases approximately linearly with height and that was compensated for by a linear increase in dwell time. The extent to which the deposited structures deviate from their design, depends on the type of structure. Open ended structures (pillars, spirals) can get heavily deformed as a result of proximity effects, but closed mesh-like structures have a much better structural integrity. In Figure 1 a few 3D-structures are shown as an example of what can be fabricated quite easily. We will discuss more structures, and issues in their fabrication, at the conference. Our aim is to inspire people to think of applications for 3D-EBID by showing our example structures.

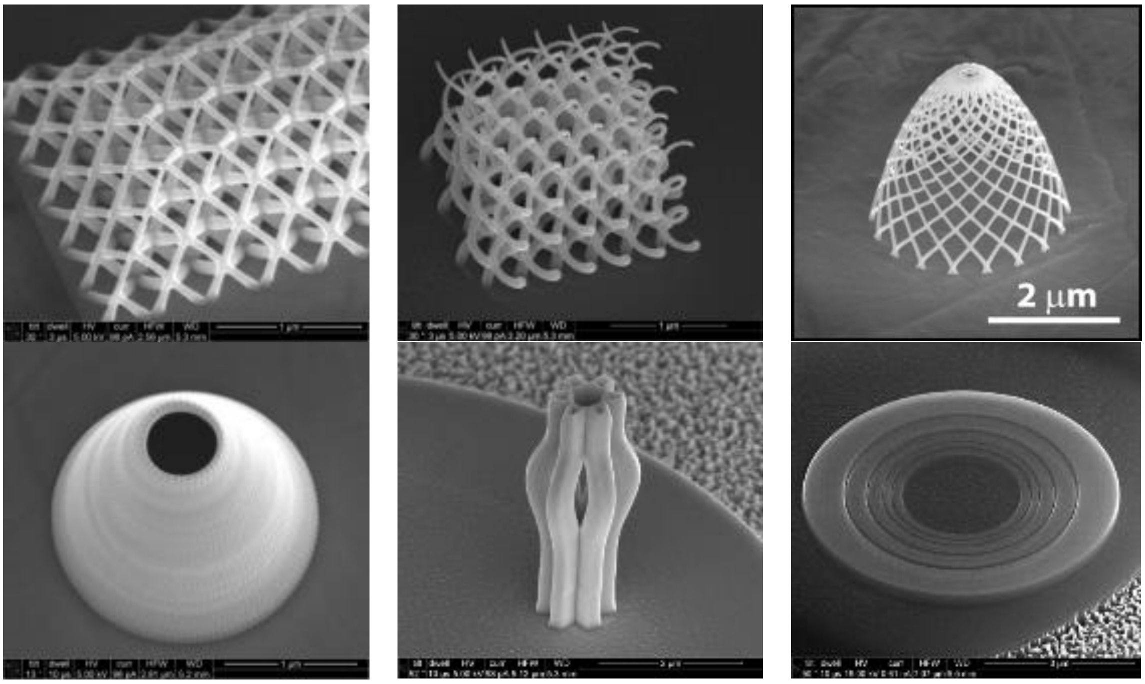

Figure 1. Examples of 3D stuctures grown by EBID using $MeCpPtMe_3$ as a precursor.

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P-15: Investigation of magnetic properties of Co/C nanostructures using MEMS devices

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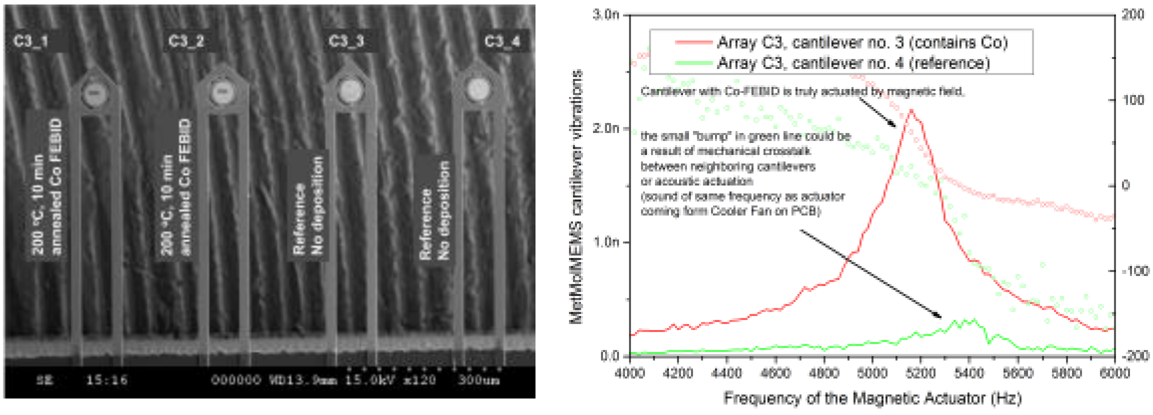
Focused electron beam (FIB) and scanning electron microscopy (SEM) enables fabrication of three dimensional (3D) structures at the locations defined with single nanometer resolution. In the focused electron beam induced deposition (FEBID) scheme the investigated structure is immersed in the gaseous environment of metal organic precursor. When exposed to the electron beam, areas of metal containing structures can be deposited. In this work, we present a method for characterization of the cobalt carbon (Co/C) nanostructures deposited on the microelectromechanical cantilever array platform. The Co/C FEBID structures exhibit magnetic properties, whose metrology, due to the small dimensions is always challenging. In our solution, we apply arrays of 4 silicon cantilevers (Fig. 1a) on which the FEBID pattern is done. The array cantilevers are fabricated in silicon on insulator (SOI) technology, which ensures that the mechanical parameters of the cantilever array are the same with an uncertainty of 5%. The stiffness and the resonance frequencies of the cantilevers are less than 0.1 N/m and 10 kHz which ensures high measurement resolution. The comparative results of the cantilever deflection measurements done with a high resolution interferometer in defined magnetic field are presented in Fig. 1b.



a b

Fig.1. The fabricated cantilevers with Co/C FEBID pattern (a) SEM image, (b) deflection comparison: with and without Co/C pattern.

Acknowledgements

The investigations of the electromagnetic actuation were done within the NCN OPUS 9 Grant - “Metrology of molecular interactions using electromagnetically actuated MEMS force sensors-MetMolMEMS” (Grant No. 2015/17/B/ST7/03876) and Wrocław University of Science and Technology statutory founding

P-16: Gas phase dissociative ionization and dissociative electron attachment to the heteronuclear FEBID precursor; $HFeCo_3(CO)_{12}$; experiment and calculations

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Low energy electron interaction with FEBID precursor molecules are getting particular attention for the last few years because of their role in determining the chemical composition and spatial resolution of structures fabricated with FEBID [1]. $HFeCo_3(CO)_{12}$ is the first bimetallic precursor molecule used in FEBID [2]. The common method to fabricate bimetallic nanostructures in FEBID is mixing different precursor molecules using dual or multichannel gas injections system [3]. However, this method has limitations with regards to the control over the deposition process and its reproducibility. The use of bimetallic precursor molecules like $HFeCo_3(CO)_{12}$ in FEBID can eliminate these limitations and hence opens a promising way to fabricate bimetallic nanostructures.

In FEBID, the deposit created from $HFeCo_3(CO)_{12}$ shows >80% metal content and the FeCo ratio was close to the stoichiometric value of 1:3. The high performance of this precursor in FEBID and the role of low energy electrons in the deposition process motivated us to conduct a low energy electron - $HFeCo_3(CO)_{12}$ interaction study in the gas phase, where an electron beam of well defined energy crosses with effusive beams of $HFeCo_3(CO)_{12}$ and the fragments formed from the electron-molecule interaction is detected using a quadrupole mass spectrometer.

In DEA to $HFeCo_3(CO)_{12}$, we observed two main channels; (i) formation of $Fe(CO)_n^-$ (n = 2 to 4) and (ii) sequential loss of CO [4,5]. The loss of 2 CO and the apex loss as $Fe(CO)_4^-$ were the most intense channels observed. The appearance energy measured for both of these channels agrees well with the corresponding thermochemical threshold calculated at PBE0/ma-def2-TZVP level of theory [5]. The most interesting feature observed in DEA to $HFeCo_3(CO)_{12}$, however, was the sequential removal of all 12 CO ligands apparent through the observation of $[M\text{-}nCO]^-$ with n = 3 - 12. These fragments are observed through discrete contributions with more number of CO lost at increasing attachment energy up to 20 eV, i.e., about 11 eV above the ionization energy of this molecule.

In dissociative ionization of $HFeCo_3(CO)_{12}$, we mainly observed fragments formed by loss of CO molecules and iron containing fragments ($Fe(CO)_n^+$ with n = 1-5). These are similar fragments observed in DEA, however, the relative intensities are distinctly different.

In the current contribution we discuss the fragmentation of $HFeCo_3(CO)_{12}$ through DEA and DI and with the support of quantum chemical calculations we seek to offer a consistent interpretation of the experimental observations.

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P-17: Elucidating the bond breaking reaction of bimetallic precursor molecule $HFeCo_3(CO)_{12}$ in FEBID using surface science experiments.

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$HFeCo_3(CO)_{12}$ is the first precursor molecule used in FEBID to fabricate bimetallic nanostructures [1]. The usual method to fabricate bimetallic nanostructures in FEBID is mixing two different precursor molecules using dual or multichannel gas injection system [2]. However, this method has difficulties to get good control over the deposits composition and reproducibility of the deposited structures. The use of heteronuclear precursors in FEBID can eliminate these difficulties.

In fact, nanostructures fabricated with $HFeCo_3(CO)_{12}$ in FEBID have shown metal content of >80% [1]. The high performance of $HFeCo_3(CO)_{12}$ in FEBID has motivated us to conduct gas phase studies [3-5] as well as studies on electron induced reaction of $HFeCo_3(CO)_{12}$ when adsorbed on a surface. In the current contribution, we discuss the electron induced surface reaction of $HFeCo_3(CO)_{12}$ monitored using XPS (X-ray photoelectron spectrometer) and mass spectrometry (MS).

From the XPS and MS data, we observed that during the initial electron induced surface reaction of $HFeCo_3(CO)_{12}$ an average of 75% of the CO ligands desorb from the adsorbed film. This results in the formation of a partially decarbonylated intermediate $HFeCo_3(CO)_x$ (x_{avg}~3). Comparison of these initial electron induced surface reactions with recent gas phase study of $HFeCo_3(CO)_{12}$ [5] indicates that the initial electron induced decomposition step proceeds through dissociative ionization rather than dissociative electron attachment. However, in FEBID, after the initial electron induced surface reaction of $HFeCo_3(CO)_{12}$ the partially decarbonylated intermediate will experience the effect of either additional electron exposure or transformations initiated by thermal instability of the intermediates. With further electron irradiation, XPS data show that the CO ligands remaining in the $HFeCo_3(CO)_x$ (x_{avg}~3) intermediate decompose into C and O. Conversely, when annealing the electron irradiated $HFeCo_3(CO)_{12}$ film, the CO ligands in the $HFeCo_3(CO)_x$ (x_{avg}~3) intermediate desorbed almost completely. Therefore, from our observations it is most likely that the deposits created from $HFeCo_3(CO)_{12}$ in FEBD will experience the following sequence of elementary reaction steps:

$HFeCo_3(CO)_{12}(ads) + e^- \rightarrow HFeCo_3(CO)_3(s) + 9CO(g)$, $FeCo_3(CO)_3(s) + \Delta \rightarrow FeCo_3(s) + 3CO(g)$.

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P-18: Investigation of $W(CO)_6$ electronic excitation by photoabsorption complemented with theoretical calculations

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High-resolution vacuum ultraviolet photoabsorption measurements of tungsten hexacarbonyl, $W(CO)_6$ in the wavelength range 115 – 320 nm (10.8–3.9 eV) have been performed at synchrotron radiation facilities in Aarhus, Denmark. Experimental measurements are complemented with comprehensive relativistic time dependent functional calculations (TD-DFT) on the low-lying excited states. The higher resolution allowed to reveal previously unresolved $W(CO)_6$ spectral features: two higher energy bands (in the energy range 7.22–8.12 eV and 8.15–9.05 eV), one of them with clear vibrational structure, and a few lower energy shoulders in addition to a couple of lower energy metal to ligand charge transfer bands reported in the literature before. Absolute photoabsorption cross sections are reported and where possible compared to previously published results. On the basis of this combined experimental/theoretical study the absorption spectrum of the complex has been re-assigned in the energy range from 3.9 and 10.8 eV [1]. The present comprehensive knowledge on the nature of the electronically excited states may be of relevance to estimate neutral dissociation cross sections from electron scattering measurements to $W(CO)_6$ a precursor molecule in focused electron beam induced deposition (FEBID) processes.

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P-19: FEBID of Single-Domain Circular Nanomagnets

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Circular magnetic nanostructures have been fabricated by focused electron beam induced deposition (FEBID) using iron pentacarbonyl $Fe(CO)_5$ as precursor. Iron deposits from this precursor have already previously been shown to be ferromagnetic [1], and the iron nanostructures in the sub-µm dimension have displayed a strong magnetic shape anisotropy [2]. This work focuses on closed iron loops of circular or elliptical shape with diameters below 2 µm. We report on the fabrication and the chemical and magnetic characterization of these circular structures.

Circular magnetic structures have been used for logic processing before the emergence of the charge-based semiconductor technology. Circular ring magnets, so-called magnetic cores, have been used to compile information via the direction of the magnetization [3]. With the emergence of nanofabrication technology also single-domain nanomagnets have become feasible and allow new applications for data storage and data processing. FEBID of magnetic nanostructures has gained recognition as a fast direct-write method for magnetic nanostructures.

Using carbonyl precursors as chemical precursors the electron-induced nanofabrication of magnetic iron and cobalt has been successfully demonstrated and high metal purities up to 100% have been achieved [5]. The ferromagnetic properties of Fe and Co deposits were confirmed [6]. Recently, also a heteronuclear Fe/Co-precursors have been used to deposit Fe-Co alloys [7]. In this work we present circular nanomagnets as building block for future magnetic devices.

With iron pentacarbonyl as precursor circular or elliptical nanostructures have been deposited. The chemical composition was strongly dependent on the precursor flux and the nozzle position. Magnetic force microscopy was used to confirm the ferromagnetic properties and the orientation of the magnetization. The effects of the circular diameter, of the thickness of the circle and the effect of shape distortion to elliptical shapes was investigated (Fig. 1).

Finally, the circular nanostructures were coupled with linear nanomagnets that have a well-defined magnetic easy axis. First results of this coupling and how it affects the magnetization type of the circular nanomagnet will be shown. Concluding, circular nanomagnets have been demonstrated to be a versatile building module for complex nanomagnetic devices.

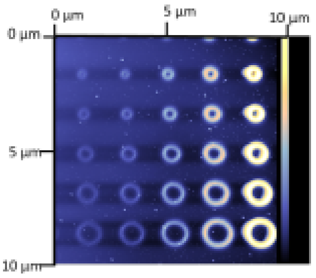

Fig. 1. AFM image of iron nanocircles deposited with different diameter and different thickness.

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P-20: Formation of formamide and isocyanic acid in condensed mixtures of carbon monoxide and ammonia

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Electron-induced chemical reactions do not only imply fragmentation of molecules as desired in FEBID but can also lead to formation of larger compounds from small starting materials. While such electron-induced synthesis is particularly relevant for fields such as astrochemistry, a comprehensive understanding of the reaction mechanisms can also help to unravel processes leading to deposit formation and purification in FEBID. Here, small molecules in the form of ligands or process gases may react with other entities of the precursor molecules either to become embedded in the deposit or to activate organic material for subsequent removal.

As a case study, this contribution reports the electron-induced formation of formamide in condensed mixtures of CO and NH_3 [1]. To provide evidence for synthesis of formamide under electron exposure, we prepared multilayer films containing equal amounts of CO and NH_3 on a tantalum (Ta) substrate at cryogenic temperatures of ~30 K under UHV conditions and subsequently irradiated these films with low-energy electrons (<20 eV). Using post-irradiation thermal desorption spectrometry (TDS), formamide ($HCONH_2$) was identified from characteristic mass over charge ratios as seen with a residual gas analyzer. The energy dependence of the product yield suggests at least two different reaction channels. In the energy regime above the ionization thresholds of NH_3 and CO, the formation of formamide is ascribed to electron impact ionization (EI) of the reactants whereas at energies below the ionization threshold, dissociative electron attachment (DEA) to NH_3 is proposed to be the dominant reaction channel.

As a by-product, isocyanic acid (HNCO) is formed in roughly equal quantities and with the same energy dependence as formamide pointing toward a common intermediate. However, the proposed reaction mechanisms for the formation of formamide initiated by EI or DEA do not provide a straightforward explanation for this finding. Therefore and also motivated by the previous result by *Zlatar et al.* that neutral dissociation (ND) may be more dominant than DEA in fragmentation of the FEBID precursor $Pt(PF_3)_4$ [2], the role of ND in NH_3 needs to be considered and effort needs to be made on how to evaluate its contributions in electron-induced synthesis.

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P-21: Towards Plug&Play Multi-Beam-EBID

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A simple add-on is developed that turns a single-beam scanning electron microscope (SEM) into a multi-beam SEM (MBSEM). The multi beam unit (MBU) can be easily inserted in the variable aperture port of a scanning electron microscope, providing *flexibility* and *versatility*, namely the changes to be made to a standard microscope do not have to be permanent and will fit easily in a variety of SEM's. The multi-electron beam unit consists of a beam splitter, a combination of a deceleration lens, a macro lens and a micro-lens aperture array. To enable individual blanking of each beam for lithography or Electron Beam Induced Deposition (EBID), a deflector array is also installed, below the beam splitter. All parts are made using microfabrication, and the entire unit fits in the 10 mm diameter variable aperture port of an SEM.

The schematics in Figure 1 shows the optical design of an SEM with a multi beam unit. First order optics calculations for such a unit in our FEI Nova-Nano-Lab 650 show that an on-axis probe size of 1.6 nm can be achieved, with 50 pA current per beam at 5 kV. Off-axis aberrations increase the outermost beam size to approximately 1.7 nm. In Figure 2, the SEM micrograph shows the stack of electrodes that form the MBU. Figure 3 shows the first array of pillars deposited by EBID using the 25 beams. The beams were not optimally focused as the diameter of the pillars is about 90 nm, as is visible from the inset in figure 3.

In this prototype version, the blanker plate is designed such that only one beam reaches the sample and therefore can be easily focused. We use a macro deflector that simultaneously deflects all the beams, that are stopped in a beam stopping aperture located underneath the objective lens, in combination with three micro deflectors, that deflect back one individual beam each. The blanker plate consists of an array of 5-by-5 apertures of 4 μm diameter at a pitch of 8.58 μm and three deflectors, each consisting of a common ground electrode and a signal electrode (see Figure 4a) that are made out of sputtered aluminium on a silicon device layer of 10 μm thickness. The insulation between the ground electrode and the signal electrode is provided by a layer of Silicon Carbide. Voltages were applied on the signal electrodes, which could hold up to 20 V, showing low leakage currents. Currently the combination of beam splitting optics and blanker plate is being tested.

We acknowledge support from the European Union under Grant Agreement No. 318804 – SNM

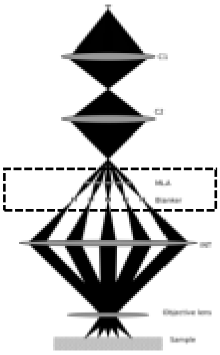

Figure 1. The design of a multi-beam SEM. The micro lens array (MLA) and blanker are indicated.

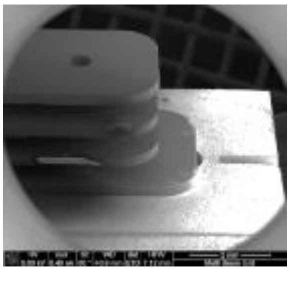

Figure 2. A SEM micrograph is shown of the stack of electrodes forming the MBU.

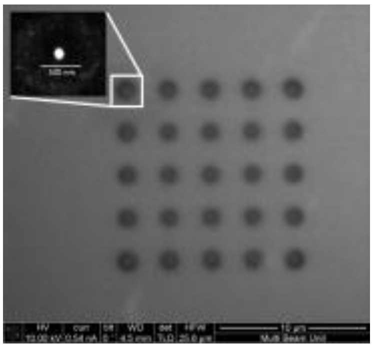

Figure 3. A 5x5 array of EBID pillars deposited in a single 5 s exposure. The inset shows a zoomed-in image of one of the pillars, with a diameter of 90 nm.

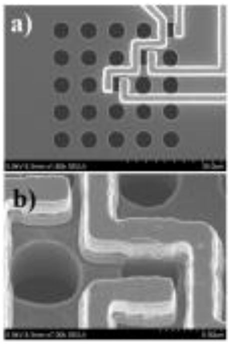

Figure 4. a) Top view SEM micrograph of the 3 micro blankers, and b) the rotated, tilted and zoomed-in view of one of the deflectors (b).

P-22: Low-energy electron interactions with $Pt(CO)_2Br_2$

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Motivated by the role of secondary electrons in focused electron beam induced deposition (FEBID) [1] we, and other research groups, have in the past studied low energy electron interactions with a number of potential and currently used FEBID precursors (*e.g.*, ref [2] and refs therein), with the aim to elucidate the role of different ligands in the decomposition process and eventually offer guidance for design of FEBID precursor molecules.

In this context, the heteroleptic complex $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ was the first halogen containing complex studied, showing potential for post deposition removal of the halogen ligand [3-5]. To explore this perspective further, gas phase and surface studies were conducted on $Pt(CO)_2Cl_2$ [6,7], which possesses a simpler ligand structure and the fairly labile carbonyl ligands.

Here we compare the higher halogen; bromine, presenting a study on decomposition of $Pt(CO)_2Br_2$ through dissociative electron attachment (DEA) and dissociative ionization (DI). The experiments were carried out in a crossed beam setup with $Pt(CO)_2Br_2$ sublimed through an effusive gas inlet, crossing a near mono energetic electron beam from a trochoidal electron monochromator. Fragment analysis and detection was carried out with a Hiden EPIC1000 quadrupole mass spectrometer.

Ion yields of 6 fragments formed by DEA from $Pt(CO)_2Br_2$ were observed, showing that DEA leads predominantly to the loss of one or both carbonyl ligands, though loss of bromine as Br^- is also appreciable. In DI at 70 eV fragmentation through the loss of one and two CO as well as the loss of one bromine and one bromine and one CO is observed with appreciable intensity, but the main fragments observed are Pt^+ and $PtBr^+$. The results are discussed in comparison with previous studies on $Pt(CO)_2Cl_2$ [6,7] and in context to the use of these compounds as Pt sources in FEBID.

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P-23: CNTs forest formation and characterization on metal deposites prepared by EBID

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Selective growth of carbon nanotubes (CNTs) at predefined positions with controlled diameter and length is an important matter in respect to their application in electronic devices. The preparation of clean and accurately positioned nanoscaled catalytic active particles is very difficult. One powerful methods is the electron beam induced deposition (EBID) of a suitable metal precursor [1,2]. This process is utilized to fabricate metal containing patterns with well-defined shape at predefined positions on SiO_x and AlO_x precovered SiO_x substrate. These EBID structures are applied as a catalyst for CNT growth by chemical vapor deposition (CVD).

Here we report on Fe and Co nanostructures (dots, squares) fabricated via EBID and subsequent autocatalytic growth (AG) in an UHV instrument using $Fe(CO)_5$ and $Co(CO)_3NO$ as precursors. It will be demonstrated that our approach is indeed successful, i.e., CNTs can be selectively grown on the latter EBID deposits. In addition the influence of the chemical composition and fabrication parameters (patterns size, electron dose and AG time) of the metal deposits was systematically investigated as well as the effect of the substrate. It will be discussed how the basic synthesis parameters were modified to successfully grow vertically aligned CNTs. Based on the SEM and EDX measurements we are also able to discuss the growth mode of CNT forests in a comprehensible way.

Overall we present and discuss a novel route towards the fabrication of well-defined CNTs with positional control.

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P-24: Theoretical study of Ag $(PMe_3)_n$ (n=2-4) as a precursor for FEBID

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FEBID can be considered as a beam-assisted chemical vapor deposition technique where the energy required to dissociate the precursor molecules is provided by electron beam irradiation, therefore the substrate is generally maintained at room temperature [1]. In this technology, the energy of the bonds in the precursor molecules must be in the range of a few eV, implying that their dissociation is generally governed by the secondary electrons produced in the substrate and the growing structure [2]. One of the most important choices of the precursors for FEBID is the chemical composition of the actual precursor molecule, i.e. the element(s) for the deposition. Other, secondary parameters follow from the choice of the precursor molecule are follows in: vapor pressure as a function of temperature, chemical stability, sticking coefficient/residence time of the precursor molecules on the sample, system behavior and practical aspects such as toxicity issues and pump out of precursor molecules after use and possible contamination of the system [3].

The aim of our study is to check does Ag $(PMe_3)_2$, Ag $(PMe_3)_3$ and Ag $(PMe_3)_4$ could be used as a precursor for FEBID taking into account that silver nanostructures have been proven to add functionality to a range of applications across many different nanotechnology sectors, from solar energy, through medical and gas sensing to food packaging. We investigate thermal and chemical stability, toxicity and the energy of the appearance of the above derivatives by B3LYP method and 3-21G and 6-31++G** basis sets for Ag and other atoms, respectively, to satisfy both accuracy of the investigations and appropriate computing time and recourses [4]. The Gaussian program package is used [5]. The values of the binding energy per atom, HOMO-LUMO gap, chemical hardness, electronegativity and the energy of the appearance of Ag are obtained and compared with those of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3) investigated experimentally to be sue that our suggested precursors satisfy the requirements of practical usage.

The results obtained indicate the decreasing of thermal stability of the compounds investigated within increasing the number of PMe_3 groups in them. The chemical stability of the $Ag(PMe_3)_3$ and $Ag(PMe_3)_2$ are lower than that of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3), what indicates the comparison of the values of chemical hardness and softness. The results of the HOMO-LUMO gap investigation prove this conclusion. Hence, the results obtained allow us to conclude that $Ag(PMe_3)_n$ (n=2-4) could not be used as a precursor for FEBID due to their low chemical stability.

Acknowledgment

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P-25: Low-energy electron interactions with the heterobinuclear FEBID precursor ($(\eta^5\text{-p})\text{Fe(CO)}_2\text{Mn(CO)}_5$)

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In recent years, a number of gas phase studies on the interaction of low energy electrons (LEEs) with organometallics have been conducted in conjunction with computational studies of these reactions [1]. Such gas phase studies can provide valuable information on the mechanisms behind deposit formation in focused electron beam induced deposition (FEBID), as well as evaluate the potential of these compounds as precursor molecules in FEBID [2,3]. Use of computational studies can give even more insight into these gas phase reactions, providing a deeper comprehension of the basic science behind them. This understanding can then be used in a variety of ways, *e.g.,* predicting behavior of similar molecules or optimizing new molecules for FEBID. Additionally, the use of heteronuclear precursors in FEBID is an attractive alternative to co-reactant precursor mixtures or multiple gas inlet systems for the fabrication of alloy nanostructures. Recent experiments with $\text{HFeCo}_3\text{(CO)}_{12}$ [4] achieved a typical metal purity of 80% with a 1:3 FeCo ratio, clearly demonstrating the viability of this approach.

Accordingly, we have conducted gas phase studies on dissociative ionization (DI) and dissociative electron attachment (DEA) to $\text{CpFe(CO)}_2\text{Mn(CO)}_5$ [5], specifically synthesized as a FEBID precursor for alloy deposition. The combination of the polyhapto cyclopentadienyl group, which is known to be a poor leaving group (ref. 4 and refs therein), and the more labile CO ligands offers an opportunity to compare these ligands in a heteronuclear architecture. Additionally, coupled cluster calculations on reaction pathways to produce the two dominant DEA fragments were performed at the DPLNO-CCSD(T) level of theory using the correlation-consistent basis sets aug-cc-pVTZ and aug-cc-pCQZ. These calculations were used to explain certain features in the DEA ion yield spectra, as well as to provide an understanding of the mechanisms producing these dominant fragments.

The two most intense fragments produced in DEA to $\text{CpFe(CO)}_2\text{Mn(CO)}_5$ are formed via a low-lying resonance leading to a maximum in the ion yield near 0 eV. These channels are the loss of one CO, and the cleavage of the iron-manganese bond to form $[\text{Mn(CO)}_5]^-$. Hence, both channels are associated with a single bond rupture. At higher energies, however, computational studies suggest that $[\text{Mn(CO)}_5]^-$ formation may proceed via decay of the $[\text{CpFe(CO)Mn(CO)}_5]^-$ fragment. Further CO loss is also observed in DEA, covering the formation of $[\text{M} - n\text{CO}]^-$ over the range from $n = 2$ to $n = 6$. These channels are orders of magnitude less efficient than the primary metal-bond rupture channels. No cyclopentadienyl loss is observed via DEA. In dissociative ionization, the fragmentation pattern observed was much more extensive compared to that observed in DEA. At about 70 eV, the DI spectra is dominated by fragments formed through the loss of 5 and 6 CO ligands, the formation of the iron cyclopentadienyl fragments FeCp and FeCp(CO)_2^+ and the bare metal ions Fe^+ and Mn^+.

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P-26: Kinetic analysis of the reaction of H radicals with HI at 298 K and very low pressures, and H_2 utilization for surface-science studies of respective FEBID precursors

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This paper summarizes the kinetics of the reaction $H + HI \rightarrow H_2 + I$ at 298°K and very low (millitorr) pressures. This represents a model reaction for studying the reactions of hydrogen radicals with hydrogen halides to yield molecular hydrogen and the respective halogen radicals. These products and/or reactants can be used as FEBID precursors either alone or in combination with other compounds. Moreover, molecular hydrogen represents a new-future source of energy and its properties and respective materials are worthy to be further studied and quantified. The mass signal intensities of I, HI, H, and H_2 were measured at 20 and 40 eV ionization potentials. Three different exit flow orifices were utilized in the reported VLPR kinetic experiments of about 2, 3, and 5 mm inner diameter to vary the measured species concentrations under steady state reaction conditions. The rate constant k_1 of the above reaction was determined and reported together with relevant parameters. Useful conclusions derived from the above research can be drawn from the use of this VLPR (very low pressure reactor) reaction technique in combination with the FEBID method and its respective techniques. Furthermore, use of hydrogen in various porous inorganic materials and membranes is under study in combination with interactions with FEBID precursors.

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P-27: Codeposition of iron and cobalt in vertical nanopillars

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Magnetic nanomaterials have received increasing attention due to their different behavior from bulk magnetic materials. In this work the codeposition of iron-cobalt in vertical nanopillars is reported. Instead of using a heteronuclear precursor two precursor gases have been injected simultaneously from two independent nozzles. As both gas fluxes can be independently regulated, the precursor gas mixture can be varied. However, with 2 precursors their different sticking probability and their different electron interaction cross section has to be considered.

Due to their strong shape anisotropy magnetic nanomaterials behave different from bulk magnetic materials. On the nanoscale the shape anisotropy allows to fabricate single domain nanostructures that can be used for a wide range of technological applications ranging from magnetic nanosensors to nanomagnet logic devices. Focused electron beam induced deposition (FEBID) has become an acknowledged method for the fabrication of 3-dimensional magnetic nanostructures. The FEBID capability to fabricate 3D nanostructures has impressively been demonstrated by Winkler [1].

The ferromagnetic properties of FEBID nanomaterials and potential nanomagnetic applications have already been extensively reported [2]. As precursor either iron carbonyls or cobalt carbonyl are most frequently used. Even in a scanning electron microscope high purities of iron [3] as well as of cobalt [4] can be achieved. With cobalt also a protective shell of platinum has been realized [5]. However, for hard magnetic applications neither iron nor cobalt but an iron-cobalt alloy with 35% Co would be the best material [6]. It is desirable to develop a deposition process for Fe-Co-alloys. Recently, a heteronuclear Fe/Co-precursor was used to deposit a Fe-Co alloy [7]. In this work we present the codeposition of Fe and Co from two individual precursors that are mixed locally at the site of deposition. This approach allows to individually adapt the Fe/Co-mixture ratio.

The two precursors iron pentacarbonyl and dicobalt octacarbonyl were injected through two separate injection nozzles into the chamber of a LEO 1530VP electron microscope. The gas fluxes into the chamber could be regulated individually, so that the setup allows to change the mixture ratio of the iron and the cobalt precursor. By irradiating the Si substrate in spot mode we performed the deposition of vertical nanopillars. Chemical analysis by SEM-EDX and TEM-EELS confirms the presence of both elements Fe and Co in the nanopillar. A detailed investigation of the elemental distribution points to a core-shell structure. It is suggested that this difference of the concentrations in the core/shell zones is due to the different sticking probabilities and the different surface diffusion rates of the precursors. The mechanism of codeposition and potential applications will be discussed.

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09:20 - 09:30		José Maria de Teresa		
09:30 - 09:50			Matija Zlatar	Anpan Han
09:50 - 10:00		Armin Gölzhäuser (Ion beam)		
10:00 - 10:20			Juraj Orzsagh	Markus Rohdenburg (STSM)
10:20 - 10:40		Teodor Gotszalk (STSM)	Anita Ribar (STSM)	Katja Höflich
10:40 - 11:10		Coffee	Coffee	Coffee
11:10 - 11:30		Iwona Szymanska	Gregor Hlawaczek (Ion beam)	Janina Kopyra
11:30 - 11:40				Sylwia Ptasinska
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12:00 - 12:10		Katarzyna Madajska (STSM)		
12:10 - 12:20			Discussion on future activites (WG meetings)	Sascha Koch
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🟦	Carboxylate precursors
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