

Kick-off Meeting COST Action CM 1301



Chemistry for EElectron-Induced NAnofabrication

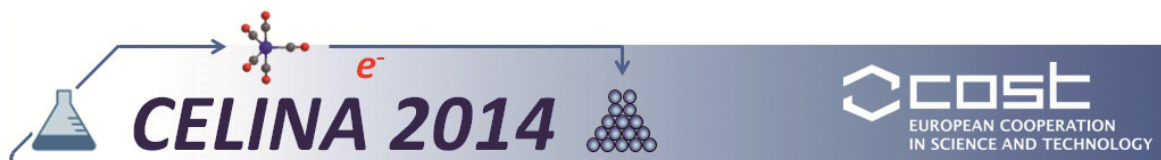
March 19-22, 2014, Erlangen, Germany

Book of Abstracts

Local Organization: PD Dr. Hubertus Marbach

Scientific Organization: Prof. Dr. Petra Swiderek





Dear participants of CELINA 2014,

we have all been brought together by the vision to advance Focused Electron Beam Induced Deposition (FEBID), an already powerful nanofabrication technique that relies on the decomposition of precursor molecules adsorbed on a surface to (hopefully!) yield the targeted material. Hopefully, because the existing precursors have not been devised to undergo precisely defined dissociation in an electron-driven process but were developed to an optimal performance in the thermally driven process of Chemical Vapour Deposition (CVD). FEBID thus urgently needs novel molecular precursors that are particularly adapted to its underlying electron-induced fragmentation mechanisms.

However, finding and tailor-making these novel substances is a challenging task.

As in CVD we need substances that contain the atoms to be deposited on a surface. This is not so difficult. But these precursors need to be volatile with a sufficient vapor pressure, stable under ambient conditions, preferably nontoxic, inexpensive...

...and they will, in the ideal case, decompose fully once a single electron interacts with them!

It is obvious that solving these challenges requires a concerted approach linking fundamental knowledge on electron-driven chemistry in FEBID with rational design and novel approaches to the chemical synthesis of these superior precursor molecules. This defines the goal that CELINA aims at and also the task of this first general meeting of our COST Action CM1301.

We have assembled here researchers from varied fields including FEBID technology, fundamental electron-induced processes, molecular synthesis, and diverse theoretical approaches relevant to the subject. This meeting gives us the platform to learn about our mutual fields, their approaches, and open questions. And we will hopefully see how we can best collaborate to the profit of this fascinating nanofabrication technology and thus make this meeting a successful one.

We also hope that you will enjoy your stay in Erlangen which developed from a small baroque university (founded 1742) town to a modern city in the “Metropolregion Nürnberg”. On different occasions you will have time for inspiring encounters, e.g., while being guided through our hosting city of Erlangen, having a good regional lunch and certainly at the conference dinner. From a scientific point of view the Cluster of Excellence Engineering of Advanced Materials (EAM) granted to the University of Erlangen with its mission statement “From Molecules to Materials” is certainly a perfect match to the planned activities of CELINA. In this regard we gratefully acknowledge financial and organizational support from the EAM for our meeting.

We wish you all a fruitful and inspiring meeting in Erlangen!

Petra Swiderek

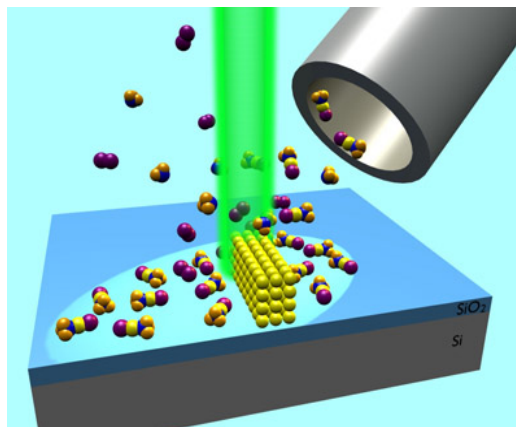
and

Hubertus Marbach

Chemistry for ELeCtron-Induced NANofabrication (CELINA)

COST Action CM1301

Electron-induced chemistry of volatile precursor molecules is central to Focused Electron Beam Induced Deposition (FEBID), a very promising direct deposition technique for nanofabrication, capable of producing free-standing 3D structures of sub-10 nm size. However, to date, FEBID relies on precursors developed specifically for chemical vapour deposition (CVD) which is a thermally driven process. These precursors are not optimized for the electron-driven FEBID process. Thus, to reach the full scientific and commercial potential of FEBID, molecular precursors particularly adapted to its underlying electron-induced fragmentation mechanisms are urgently needed.



Research aiming at improved FEBID precursors requires a concerted approach linking fundamental knowledge on electron-driven chemistry in FEBID with rational design and chemical synthesis of novel, superior precursor molecules. The COST Action CELINA networks the relevant research communities including both experiment and theory. It thus performs the fundamental research on the electron-induced reactions of FEBID precursors and translates the generated knowledge to novel and superior precursors.

Participation of research groups in FEBID technology and industrial partners will further allow rapid transfer of the results into industrial processing. This unique programme will ensure that EU academia and industry remain the leaders in development and commercial exploitation of FEBID.

More information about COST Action CELINA:

- [Memorandum of Understanding](http://www3.cost.eu/fileadmin/domain_files/CMST/Action_CM1301/mou/CM1301-e.pdf):
www3.cost.eu/fileadmin/domain_files/CMST/Action_CM1301/mou/CM1301-e.pdf
- [COST Action CM1301](http://www.cost.eu/domains_actions/cmst/Actions/CM1301): www.cost.eu/domains_actions/cmst/Actions/CM1301
- [CELINA home](http://celina.uni-bremen.de/celina/celina2014): http://celina.uni-bremen.de/celina/celina2014



Cluster of Excellence

Engineering of Advanced Materials (EAM)

The vision of the Cluster of Excellence Engineering of Advanced Materials (EAM) is to link, in the context of a world-class research and training program, fundamental science and real-world applications in the field of high-performance materials. The FAU's unique combination of strengths in engineering and natural science leads to the scientific concept of EAM, which focuses on the science and engineering of hierarchical materials organized from nano- to macroscopic scales. Bridging the gap between nanoscale materials design and macroscopic devices ("from molecules to materials to functions") requires approaches that can cover the entire range of time and length scales in synthesis and processing, modeling and simulation. These approaches must be developed coherently with structure, property and process analytics. EAM's scientific structure reflects its research philosophy. It consists of three cross-sectional areas organized in sustainable interdisciplinary centers for Functional Particle Systems, Nanoanalysis and Microscopy and Multiscale Modeling and Simulation, and four Research Areas organized in process chains: engineering of Nanoelectronic Materials, Photonic and Optical Materials, Catalytic Materials and Lightweight Materials.

www.eam.fau.de

Program

Thursday, March 20, 2014

9.00 - 9.20	Hubertus Marbach Petra Swiderek	Welcome Chemistry for Electron-Induced Nanofabrication
9.20 - 9.50	Ivo Utke	Chemistry for Focused Electron Beam Induced Deposition
9.50 - 10.30	Oddur Ingólfsson	Dissociative electron attachment and dissociative ionization in FEBID; comparison of gas phase and surface studies on selected precursor molecules
10.30 - 11.00	<i>Coffee break</i>	
11.00 - 11.30	Hans Mulders	The ideal precursor: an industry perspective
11.30 - 12.00	Markku Leskelä	Volatile Precursors: Keys for Deposition of Thin Films by Chemical Gas-phase Techniques
12.00 - 12.30	Hubertus Marbach	Lithographic fabrication of clean nanostructures via Electron Beam Induced Surface Activation: new perspectives and challenges for precursor chemistry
12.30 - 14.30	<i>Lunch break in restaurant "Alter Simpl"</i>	
14.30 - 14.50	Patrik Hoffmann	Are Halides and/or Hydrides Ideal FEBIP Precursors?
14.50 - 15.10	Iwona Szymańska	Electron-Impact Mass Spectrometry of Copper and Silver Carboxylate Compounds
15.10 - 15.30	Andrey Solov'yov	MBN Explorer - a powerful, universal tool for simulating multiscale complex molecular structure and dynamics: morphological transitions of nanostructures
15.30 - 16.00	<i>Coffee break</i>	
16.00 - 18.30	Poster and Discussion Session	
17.30 - 18.30	parallel MC meeting	
18.30 - 19.30	<i>Dinner buffet at conference site</i>	
19.30 - open end	Further discussions / poster presentations	

Friday, March 21, 2014

9.00 - 9.30	Roser Valenti	Electron-beam-induced-deposition of nanostructures: an overview on microscopic modeling
9.30 - 10.00	Willem van Dorp	A study of gold complexes for focused electron beam induced deposition
10.00 - 10.30	Heinrich Lang	The Design of Metal-Organic Precursors for Gas Phase Deposition Processes
10.30 - 11.00	<i>Coffee break</i>	
11.00 - 11.30	Roman Čurík	Electron-molecule interactions in FEBID through eyeglasses of scattering theory
11.30 - 11.50	Janina Kopyra	Electron driven processes in cisplatin
11.50 - 12.10	Sven Barth	Precursor Design for Vapor-Phase Growth of Inorganic films
12.10 - 12.30	Juraj Fedor	Electron-induced dissociative processes in FEBIP precursors and related molecules
12.30 - 14.00	<i>Lunch break and discussion at conference site</i>	
14.00 - 14.30	Maciej Gutowski	Electron-Initiated Proton Transfer in Molecular Systems
14.30 - 14.50	Richard Palmer	Non-local manipulation of polyatomic molecules in the STM
14.50 - 15.10	David Field	The spontelectric nature of films; implications for FEBID
15.10 - 15.30	Petra Swiderek	Concluding discussion and work plan
15.30 - 16.00	<i>Coffee break</i>	
16.00 - 17.30	WG meetings with further time for scientific discussions and conclusion of MC meeting	
18.00 - open end	<i>Guided tour to Erlangen and conference dinner in restaurant "Mein lieber Schwan"</i>	

Abstracts

Invited and contributed talks

Chemistry for Electron-Induced Nanofabrication

Petra Swiderek

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Electron-induced chemistry of volatile precursor molecules is central to Focused Electron Beam Induced Deposition (FEBID), a direct deposition technique capable of fabricating free-standing 3D structures of sub-10 nm size [1]. In FEBID, a tightly focused high-energy electron beam impinges onto a surface exposed to a continuous stream of precursor molecules which decompose through electron-molecule interactions to form, in the ideal case, a chemically and structurally well-defined (e.g. pure metal) deposit while volatile fragments are pumped away. To date, FEBID relies on precursors developed for chemical vapour deposition (CVD), a thermally driven process. These are not optimal for the electron-driven FEBID process. Typical FEBID deposits thus have purities of only 15-75% and deposit widths are often a multiple of the beam diameter.

It is obvious that FEBID needs novel precursors that are adapted to electron-induced fragmentation mechanisms. Although the energy of the primary electron (PE) beam in FEBID is in the 10's of keV range, the bulk of the chemical reactions are initiated by low energy secondary electrons (LESEs) released in large numbers under the PE beam and exiting the material also outside the beam focus. LESEs typically have energies below 50 eV with distributions peaking well below 10 eV. In this range, electrons fragment molecules by both dissociative electron attachment (DEA) and dissociative ionization (DI) [2]. These processes must be understood in detail to identify strategies towards improved precursors. In conclusion, we need a concerted approach that links knowledge on electron-driven chemistry in FEBID with rational design and chemical synthesis of novel precursor molecules. COST Action CM1301 (CELINA) [3] will network the relevant research communities towards a successful development of novel FEBID precursors.

[1] I. Utke, P. Hoffmann, J. Melngailis, *J. Vac. Sci. Technol. B* **26** (4), 1197 (2008).

[2] J.H. Moore, P. Swiderek, S. Matejcek, M. Allan, in *Nanofabrication using focused ion and electron beams: Principles and applications*, P. Russell, I. Utke and S. Moshkalev (Eds.), Oxford University Press, New York (2012), pp. 184.

[3] <http://celina.uni-bremen.de/celina/>

Chemistry for Focused Electron Beam Induced Deposition

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The control of products from electron triggered adsorbate dissociation reactions takes the pole position in the wish list of further development in focused electron beam induced processing (FEBIP) [1,2]. These electron triggered dissociation reactions have been recognized to be often distinctly different in deposit composition to thermal dissociation or dissociative chemisorption mechanisms prevailing for volatile molecules designed for chemical vapor deposition (CVD) or atomic layer deposition (ALD) techniques. Figure 1 schematically illustrates various possible dissociation pathways: complete dissociation (1a) would be the most desired pathway which removes all the ligands and leaves only the central atom as deposit. Incomplete dissociation (1b) [3] or ligand codeposition (1c) are the more frequently observed pathways for organometallic compounds, leaving the central atom together with a matrix of ligand elements. The addition of gases (1d) allows a greater control of deposit composition and can be used to remove part of the co-deposited ligand elements [4].

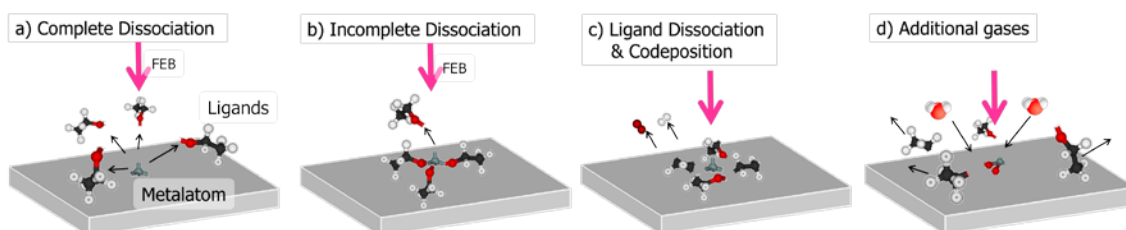


Figure 1: Schemes of electron triggered dissociation reactions leading to different products and deposit composition. a) to c) is for one adsorbate species while d) involves an additional gas, like H₂O becoming reactive when irradiated with electrons.

We will shortly review the use of molecules in FEBIP and their dissociation products and discuss further mechanisms which may play a role in purity: surface activation [5], auto-catalysis, and background residual gases.

- [1] I. Utke and A. Götzhäuser, Highlight Article, *Angew. Chem. Int. Ed.* **49** (2010) 9328 – 9330.
- [2] L. Bernau, M. Gabureac, R. Erni, I. Utke. *Angew. Chem. Int. Ed.* **49** (2010) 8880 – 8884.
- [3] J.D. Wnuk, W.F. Van Dorp, C.W. Hagen, D.H. Fairbrother et al., *Surface Science* **605** (2010) 257-266.
- [4] I. Utke, P. Hoffmann and J. Melngailis, Review, *J. Vac. Sci. Technol. B* **26** (2008) 1198-1276.
- [5] M.-M. Walz, M. Schirmer, H. Marbach et al., *Angew. Chemie Int. Ed.* **49** (2010) 4669-4673.

Dissociative electron attachment and dissociative ionization in FEBID; comparison of gas phase and surface studies on selected precursor molecules.

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Currently, the main challenges in further advancing FEBID as an industrial processing tool are to achieve better control of the composition and purity of the deposits and to further improve the spatial resolution. While contamination of the deposit is mainly attributed to incomplete decomposition of precursor molecules, co-deposition of ligands, and contamination from residual gases, broadening of the structures is generally attributed to electron flux outside the focus point of the primary beam. By and large, these effects are mainly ascribed to low energy secondary electrons (SE) and backscattered electrons (BSE) that are produced through elastic and inelastic scattering of the primary electron beam.

The SEs are generally abundant and their energy distribution peaks well below 10 eV. In this energy range the only efficient fragmentation mechanism is DEA. This is a resonant process that can be very efficient and causes mainly incomplete dissociation, and may thus potentially contribute significantly to the deposition of non-metal contaminants. DI, on the other hand, is non-resonant, but can nonetheless be very effective at low incident energies (10–50 eV). It may thus also contribute significantly to adverse effects, especially to broadening of the deposit.

In an attempt to give some insight into the dissociation mechanisms relevant to FEBID, gas phase DEA and DI results on typical FEBID precursors are compared in the current contribution and brought into context with surface science studies on the decomposition of the same molecules when these are adsorbed on a substrate and exposed to high energy electrons. Specifically, results on the precursor molecules $\text{Co}(\text{CO})_3\text{NO}$ [1], MeCpPtMe_3 [2], and $\text{Pt}(\text{PF}_3)_4$ [3] will be reviewed.

1. Engmann et al. *Angew. Chem. Int. Ed.* 2011, **50**, 9475, Engmann et al. *J. Chem. Phys.* 2013, **138**, 044305 and Rosenberg et al, *J. Phys. Chem. C*, 2013, **117**, 16053
2. Engmann et al. *Phys. Chem. Chem. Phys.*, 2012, **14**, 14611, van Dorp et al *J. Appl. Phys.*, 2009, **106** and Wnuk et al. *J. Phys. Chem. C*, 2009, **113**, 2487-2496.
3. M. Allan, *J. Chem. Phys.*, 2011, **134**, 204309 May et al. *Phys. Chem. Chem. Phys.*, 2012, **14**, 2979 and Landheer, et al, *J. Phys. Chem. C*, 2011, **115**, 17452-17463.

The ideal precursor: an industry perspective

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Currently many different precursors are used for the electron beam induced deposition process. Many of these can be found in regular CVD precursor lists from the major chemical companies and a few have been synthesized in small quantities for testing. The main and most obvious requirement for a precursor is the presence of the desired element such as Co or Fe for the creation of magnetic structures, Pt and W for conductive structures and Au for optical or bio-active structures. The second requirement is that the precursor selected can be applied in an EBID process to produce sufficient purity for the purpose aimed for. No doubt that meta-materials, containing Pt or W -grains in a carbonous matrix, are interesting materials, but the application area for direct deposition of pure enough materials is larger.

The scope of the CELINA project is focused around this central theme. However, the number of requirements for a good precursor is much larger. The transition from solid or liquid phase into vapor phase is an essential one (see example in figure 1), as well as the stability of the chemical and the level of vapor pressure. Also the toxicity and compatibility with the microscope environment are very important factors. Another important characteristic of a precursor is its disappearance from the environment after it has been used – the decay of the deposition as a function of time. In the end all precursors will be pumped out by the system but if the time between use as a deposition material and the use of the microscope as an imaging tool gets too long, the precursor is no longer practical. So although the main focus is on purity of material and new functional precursors, the list of characteristics to take into account is larger and will be discussed in more detail.

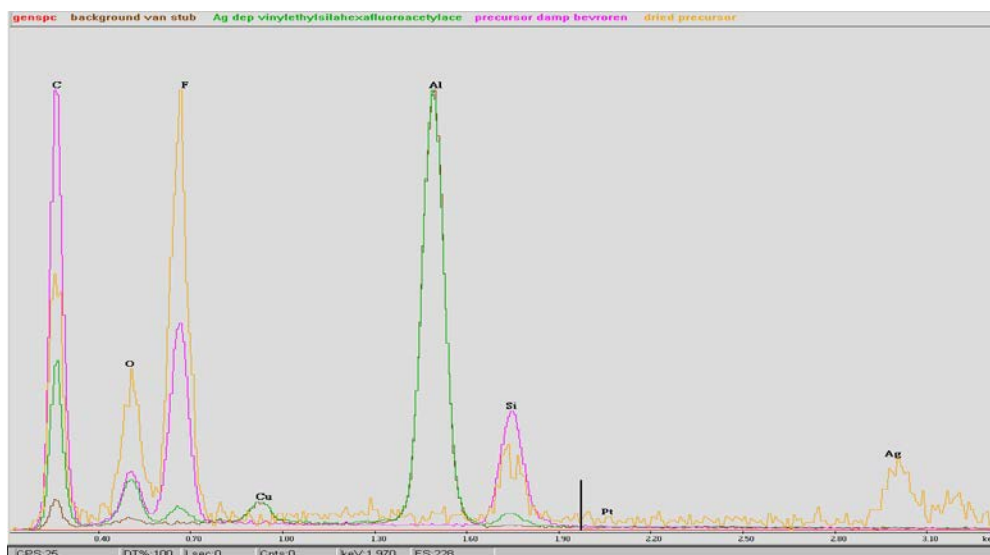


Figure 1: Response of a Ag precursor candidate –vinylethylsilahexafluoroacetylacetonate- that did produce a deposition and at a good rate. However, the Ag was missing in the actual deposit (all lines but the orange one), meaning that the original precursor did not go from solid phase to vapor phase, but instead transferred into another molecule with no Ag, but all other elements present in the precursor.

Volatile Precursors: Keys for Deposition of Thin Films by Chemical Gas-phase Techniques

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Chemical gas-phase thin film deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) rely on volatile precursors and their reactions on substrate surface. Very many types of metal precursors have been developed for CVD and ALD. They can be grouped in inorganic, metal organic and organometallic compounds. Halides are the most common volatile inorganic complexes and they have widely been used in deposition of oxide, nitride, and chalcogenide films. Alkoxides, β -diketonates and alkyl amides are probably the most common metal-organic precursors containing organic ligand but not having a metal-carbon bond. The most common organometallic precursors are carbonyl, alkyl, cyclopentadienyl and allyl compounds. Thermal stability of the metal precursors varies a lot and the stability determines if the precursor can be used in CVD or ALD since ALD requires thermally stable precursors. The reactivity of the metal precursor depends of course on the non-metal precursor. The non-metal precursors vary depending on the desired film material: for oxides water or oxygen, for nitrides ammonia, for carbides different hydrocarbons are used. Hydrides of the group 15 and 16 compounds are used for phosphide, arsenide, antimonide, sulfide, selenide, and telluride films. The deposition of metal films requires usually the use of reducing agents, only platinum group metals can be deposited using oxygen as the non-metal precursor. The reactivity and stability of the metal complexes can be tuned by heteroleptic complexes, *i.e.* complexes containing two or more ligands. In the presentation different precursors and reaction types as well as possibilities to tailor the precursor properties will be discussed.

Lithographic fabrication of clean nanostructures via Electron Beam Induced Surface Activation: new perspectives and challenges for precursor chemistry

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With the availability of localized electron probes, e.g., in scanning electron microscopy (SEM), it became possible to apply electron induced processes on the nanometer scale. Thus, in Focused Electron Beam Induced Processing (FEBIP) the generation of extremely small, pure nanostructures can be targeted with lithographic control. The most prominent FEBIP technique is Electron Beam Induced Deposition (EBID) in which adsorbed precursor molecules are locally dissociated by the impact of the electron beam leaving a deposit of the non-volatile dissociation products on the surface [1, 2]. Recently, we were able to expand the family of FEBIP techniques with the exploration of Electron Beam Induced Surface Activation (EBISA) [3-5]. Thereby, in a first step, the chemical properties of the surface itself are modified via the e-beam, such that it becomes active towards the decomposition of certain precursor molecules. In a second step, the surface is exposed to the precursor which decomposes at the preirradiated areas and eventually continues to grow autocatalytically. We demonstrate the feasibility of EBISA with $\text{Fe}(\text{CO})_5$ for different oxide surfaces, e.g. $\text{TiO}_2(110)$ [4] (Fig. 1) and silica [3] and expand it to porphyrin layers on $\text{Ag}(111)$ [5]. With our specific “surface science” approach to FEBIP, we are able to fabricate clean metallic deposits with both EBID and EBISA [2-5]. It is clear that the demands for correspondingly optimized precursor molecules are different in EBISA (or more generally the catalytic growth) than in EBID. The underlying physical/chemical processes, in particular the corresponding catalytic effects in EBISA, will be discussed with an emphasis on the precursor chemistry.

- [1] van Dorp, W. F.; Hagen, C. W., *J. Appl. Phys.* 104, 081301 (2008); Utke, I.; Hoffmann, P.; Melngailis, J., *JVST B*, 26, 1197 (2008); I. Utke, A. Götzhäuser, *Ang. Chem. Int. Ed.*, 49, 9328 (2010)
- [2] Lukaszcyk, T., M. Schirmer, H.P. Steinrück, and H. Marbach, a) *SMALL*, 4, 841 (2008) and b) *Langmuir*, 25, 11930 (2009)
- [3] M.-M. Walz, M. Schirmer, F. Vollnhals, T. Lukaszcyk, H.P. Steinrück, and H. Marbach, *Ang. Chem. Int. Ed.*, 49, 4669 (2010) and *PCCP*, 13, 17333 (2011), M.-M. Walz, F. Vollnhals, F. Rietzler, M. Schirmer, H.P. Steinrück and H. Marbach, *App. Phys. Lett.*, 100, 053118 (2012).
- [4] F. Vollnhals, T. Woolcot, M.-M. Walz, S. Seiler, H.P. Steinrück G. Thornton and H. Marbach, *J. Phys. Chem. C*, 117, 17674 (2013)
- [5] F. Vollnhals, P. Wintrich, M.-M. Walz, H.P. Steinrück and H. Marbach, *Langmuir*, 29, 12290 (2013)
M.-M. Walz, F. Vollnhals, F. Rietzler, M. Schirmer, H.P. Steinrück and H. Marbach, *Appl. Phys. Lett.* **100**, (2008). 053118

Are Halides and/or Hydrides Ideal FEBIP Precursors ?

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Deposition or co-deposition of unwanted material is still the major challenge for FEBIE and FEBID. Process parameters optimization can reduce but not avoid unwanted deposits. This contribution will try to give the main reasons for, and propose potential solutions to the problem.

The FEBID process can be seen that adsorbed precursor molecules exposed to dense fluxes of electrons do undergo multiple excitations of various types. The “precursor” molecule under irradiation becomes a loose agglomeration of atoms and molecular fragments resulting in different deposits as function of the parameters. The following rules are presented and will be explained:

Avoid atoms in the ligands that are elemental solids

Choose atoms in/for the ligands from which the elements are gases

- but avoid existing very stable and electron resistant compound formation (SiO_2)

Avoid residual water in the chamber

If using precursors violating rules 1 and 2, find self decomposition catalyzing precursors

Following these rules, halides and hydrides are, together with real dry reactors, prerequisite conditions for “pure” deposit from FEBID.

The conclusion from this analysis is that toxic, corrosive, or pyrophoric compounds are/would be the ideal precursors for FEBIP. The in-situ production on demand of such compounds in close proximity to the substrate, [1] with well thought recovery of by-products and unreacted precursor and its in-situ neutralization would be the ultimate solution for high quality pure deposition of a variety of materials.

[1] B. Afra, PhD thesis, EPFL, 2011

Electron-Impact Mass Spectrometry of Copper and Silver Carboxylate Compounds

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Copper exhibits electrical conductivity higher than aluminum and relatively good electromigration resistance. Silver has the highest electrical current and heat conductivity. Therefore, both metals are extensively used in microelectronics. Bimetallic composites Cu/Ag can be alternative materials, used as interconnections. Moreover, silver and copper antibacterial properties imply the production of aseptic coatings.

In the case of $[\text{Cu}_n(\text{CH}_2=\text{C}(\text{H})\text{SiR}'_3)_n(\mu\text{-O}_2\text{CR})_n]$ compounds the binuclear $[\text{Cu}_2(\text{O}_2\text{CR})]^+$ and the next $[\text{Cu}_2(\text{O}_2\text{CR})_2]^+$ fragments achieved the highest intensity among metallated ions ($\text{R}' = \text{Me}, \text{Et}, \text{OMe}$; $\text{R} = \text{CF}_3, \text{C}_2\text{F}_5$).^[1] For the $[\text{Cu}_2(\text{VTXS})_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ compounds the relative intensity of the signals was significantly higher than for the trifluoroacetates. Moreover, the initial vaporisation temperature of them was lower which suggested that these compounds would be more promising for the CVD process. The $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{CR})_4]$ complexes were the source of the different metallated fragments.^[2] The registration of the pseudomolecular $[\text{Cu}_2(\text{O}_2\text{CR})_3(\text{tBuNH}_2)_2]^+$ ion also in the case of the long-chaining carboxylate $\text{C}_6\text{F}_{13}\text{CO}_2$ indicates the high stability of the complexes in the gaseous phase. Moreover, in the mass spectra the $[\text{Cu}_3(\text{O}_2\text{CR})_5]^+$ fragment was detected and theoretical calculations were performed for its structure determination.

Furthermore, systems of the $[\text{Ag}(\mu\text{-O}_2\text{CC}_2\text{F}_5)]_n / [\text{Cu}_2(\text{VTMS})_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ compounds were studied. The temperature separation between the high intensity region of the carboxylate $[\text{Ag}_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$ and $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$ fragments is larger for the precursor system than for the pure precursors and bimetallic $[\text{AgCu}(\text{O}_2\text{CC}_2\text{F}_5)_x]^+$ were also observed.^[3]

[1] I.B. Szymańska*, P. Piszczek, E. Szlyk, *Polyhedron*, 28 (2009) 721-728.

[2] I.B. Szymańska*, *Polyhedron*, 50 (2013) 200-207.

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

**MBN Explorer - a powerful, universal tool for simulating multiscale
complex molecular structure and dynamics:
morphological transitions of nanostructures**

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MBN Explorer [1] is a multi-purpose software package designed to study structure and dynamics of molecular systems of various degrees of complexity. A broad variety of interatomic potentials implemented in the MBN Explorer allows to simulate the structure and dynamics of different molecular systems, such as atomic clusters [3], fullerenes [4], nanotubes and nanowires [5], metallic nanomaterials [6], proteins and DNA [7], crystals [8], composite bio-nano systems and nanofractals [9]. A distinct feature of the package, which makes it significantly different from other codes, is its universality, implemented multiscale features and applicability to a broad range of problems and complex molecular systems.

The talk will give an overview of the main capabilities of the package and its computational efficiency. The following case studies will be highlighted:

- ❖ Rayleigh instability of free and deposited nanosystems (nanoparticles and nanowires)
- ❖ Monte-Carlo simulations of atomic cluster deposition, nanofractal growth and thermally induced morphological transition of nanofractals.

Detailed information about MBN Explorer can be found on the dedicated website [2]. Currently, there are more than 1000 registered users of MBN Explorer. MBN Explorer has been developed under the auspices of Virtual Institute on Nano Films. The reported case studies have been conducted at the Frankfurt Institute for Advanced Studies.

[1] A.V. Solov'yov *et al*, *J. Comp.Chem.* **33**, (2012) 2412

[2] A.V. Verkhovtsev *et al*, *Computational Materials Science* **76** (2013) 80

[3] J. Geng J, I.A. Solov'yov *et al*, *Phys. Rev. B* **81** (2010) 214114

[4] I.A. Solov'yov *et al*, *Phys. Rev. E* **78** (2008) 051601

[5] A.V. Verkhovtsev *et al*, *Computational Materials Science* **76** (2013) 20

[6] E. Surdutovich *et al*, *Sci. Rep.* **3** (2013) 1289

[7] G B Sushko *et al*, *Journal of Computational Physics* **252** (2013) 404

[8] V.V. Dick *et al*, *A V Phys. Rev. B* **84** (2011) 115408

Electron-beam-induced-deposition of nanostructures: an overview on microscopic modeling

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Electron-beam-induced deposition (EBID) of precursor molecules on a substrate is a widely used technique in the mask-free growth of nanostructured materials, a subject of relevance both for fundamental physics and chemistry and for industrial applications. Despite the widespread use of this technique, a detailed theoretical description of the full EBID process is still missing. This is due to the complex interplay of the multiple physical and chemical processes involved. In this presentation I will give an overview on the processes involved in EBID and will discuss the various theoretical approaches currently considered in order to describe EBID.

A study of gold complexes for focused electron beam induced deposition

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It sounds so simple. You put a sample in a scanning electron microscope, direct a flow of gas to it and you can use the electron beam as a pen. At the sample surface, the electrons crack the (adsorbed) gas molecules and you can use the solid residue that remains on the surface as ink. In this way you can write for instance free-standing 3D structures, magnetic tips for scanning probe microscopy, nanowires, electrodes, etc [1]. But the precursors used for the deposition typically yield material of inferior quality. In large part this is because the precursors are chosen from catalogues for atomic layer deposition or chemical vapor deposition.

However, electron-induced chemistry is significantly different from chemistry between neutrals. For instance, while carbocyclic ligands are removed easily in thermal chemistry, it is very difficult to remove them with electrons [2]. This suggests that we have to move away from such (relatively large) organic ligands if we want to develop novel precursors for electron-induced chemistry. Small and potentially volatile ligands appear to be more promising.

Our aim is to gain control over the deposition process and obtain sufficient information to design and synthesize new precursors for electron-induced chemistry. We start our study with a preliminary exploration of four gold complexes: chloro-gold(III)-dimethyl ($\text{Cl-Au}^{\text{III}}\text{-Me}_2$) [3], chloro-gold(I)-dimethylsulfide ($\text{Cl-Au}^{\text{I}}\text{-SMe}_2$) [4], chloro-gold(I)-trimethylphosphine ($\text{Cl-Au}^{\text{I}}\text{-PMe}_3$) [5] and methyl-gold(I)-trimethylphosphine ($\text{Me-Au}^{\text{I}}\text{-PMe}_3$) [5].

All four complexes are solids at room temperature and their vapor pressure is high enough to be used as precursor. The crystals are characterized with energy-dispersive X-ray spectroscopy (EDS). The volatile components are analyzed with mass spectrometry and X-ray photoelectron spectroscopy. The suitability of the complexes for focused electron beam induced deposition is tested on a dual beam system. The composition of the deposits is determined with EDS.

[1] I. Utke, P. Hoffman, J. Melngailis, *J. Vac. Sci. Technol. B* **26** (2008) 1197

[2] J..D. Wnuk, S.G. Rosenberg, J.M. Gorham, W.F. van Dorp, C.W. Hagen, D.H. Fairbrother, *Surf. Sci.* **605** (2011) 257

[3] R.S. Tobias, W.M. Scovell, G.C. Stocco, *Inorg. Chem.* **9** (1970) 2682

[4] P. G. Jones, J. Lautner, *Acta Cryst. C* **44** (1988) 2089

[5] H. Schmidbaur, A. Shiotani, *Chem. Ber.* **104** (1970) 2821

The Design of Metal-Organic Precursors for Gas Phase Deposition Processes

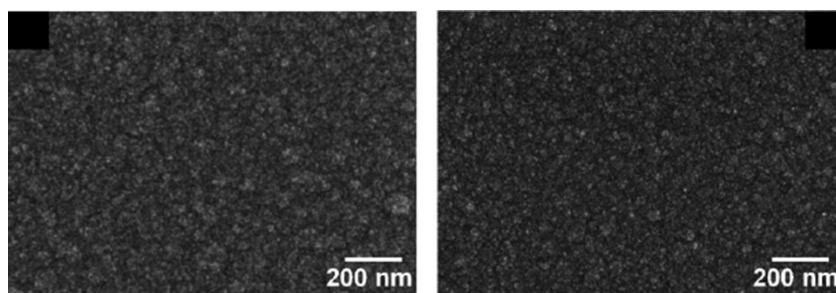
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Recently, the metal-organic chemical vapor deposition (MOCVD) of metals was studied intensively because this gas-phase deposition technology is advantageous compared to physical vapor deposition, since MOCVD allows the efficient formation of pure, crystalline, conformal and closed metal thin layers. [1]

One of our group topics deals with the specific design of novel, volatile MOCVD precursors for conductive, semi-conductive and magnetic layer formation. We herein present a coordinated approach for precursor design, their characterization and their systematic use as CVD precursors for thin metal film fabrication on the example of Ag and Ru layer growth. For pure Ag layer formation the use of the metal-organic silver(I) complexes $[\text{Ag}(\text{O}_2\text{CR}')(\text{R}_3\text{P})_n]$ (R, R' = organic ligand; $n = 0, 1, 2, 3$) as CVD precursors will be described. [2] The organic groups R and R' in coherence with the number n of the coordinated Lewis-base ligands PR_3 do have a great influence on the decomposition parameters and hence on the layer formation process, which also will be highlighted. This strategy will also be explained by using Ru-carboxylates, Ru-half-open sandwich and Ru-sandwich complexes as suitable MOCVD precursors for the generation of pure and conformal thin Ru layers. [3]



SEM images of Ru films generated from $[\text{Ru}(\eta^5\text{-C}_5\text{H}_3\text{tBuSiMe}_3)(\eta^5\text{-C}_5\text{H}_4\text{tBu})]$ (left) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_3\text{tBuSiMe}_3)_2]$ (right). [3]

- [1] H. Lang, S. Dietrich, *In Comprehensive Inorg. Chem. II: From Elements to Applications*, **4** (2013) 211–269.
- [2] T. Haase, K. Kohse-Höinghaus, N. Bahlawane, P. Djiele, A. Jakob, H. Lang, *Chem. Vap. Deposition* **11** (2005) 195–205.
- [3] A. Tuchscherer, C. Georgi, N. Roth, D. Schaarschmidt, T. Ruffer, T. Wächter, S. E. Schulz, S. Oswald, T. Gessner, H. Lang, *Eur. J. Inorg. Chem.* (2012) 4867–4876.

Electron-molecule interactions in FEBID through eyeglasses of scattering theory

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I will attempt to summarize various theoretical approaches that are presently being used to model elastic and inelastic electron-molecule collisions. The focus will be placed on theoretical methods that are at disposal of the COST Action CM1301 and processes that can be treated by these methods. First, I will outline high-energy regime (~ 1 keV) modeling via IAM-SCAR method [1] and then I will concentrate on low-energy processes (1-20 eV) that may be initiated by secondary electrons. In particular, resonances play an essential role in electron-induced fragmentation mechanisms. Therefore I will describe their identification in fixed-nuclei computation with UK Molecular R-matrix Codes [2] and also how the resonances exhibit themselves in vibrationally inelastic calculations [3].

The information that can be obtained by theoretical scattering methods will be demonstrated on examples of polyatomic molecules.

[1] A.G. Sanz, M.C. Fuss, F. Blanco, F. Sebastianelli, F.A. Gianturco and G. Garcia, *J. Chem. Phys.* **137** (2012) 124103

[2] Z. Masin and J.D. Gorfinkiel, *J. Chem. Phys.* **137** (2012) 204312

[3] R. Čurík, P. Čársky and M. Allan, *Phys. Rev. A* **86** (2012) 062709

Electron driven processes in cisplatin

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Pt-precursors are widely used in medical applications [1] as well as in deposition techniques in order to form nanometer structures. Recently, attention has been paid to trimethyl (methylcyclopentadienyl) platinum (IV) ([MeCpPt(IV)Me₃]) typical precursor used for the deposition of metallic nanostructures. Here we present results of low energy electron attachment to cisplatin (*cis*-diamminedichloroplatinum(II), Pt(NH₃)₂Cl₂) obtained by means of a crossed beams apparatus. Such electrons are generated with a high efficiency as a secondary species having initial energies in the range of a few tens of eV [2].

Dissociative electron attachment (DEA) to cisplatin [3] shows intense resonances at very low energies (close to zero eV) resulting in Pt-Cl bond cleavages. Effective cleavage of this single bond is visible via the appearance of the two complementary fragments namely Cl⁻ and (M-Cl)⁻ ((Pt(NH₃)₂Cl)⁻). While the (M-Cl)⁻ anion appears as a single resonance, the Cl⁻ anion is generated via two closely spaced features both at energy below 1 eV. Apart from these products we observe a strong reaction resulting in the loss of two Cl atoms thereby forming either Cl₂⁻ or (Pt(NH₃)₂)⁻ anion. It is worth noting that the maximum count rate of (Pt(NH₃)₂)⁻ is more than 25 times that of Cl₂⁻. The only structure that appears at higher energy domain, between 5-6 eV, is formation of NH₂⁻. The shape and the position of the fragment resemble that of NH₂⁻ from ammonia, thus we suggest that it is generated from localisation of the excess charge at the coordinatively bound ammonia molecule.

[1] V. Brabek, in *Platinum-based drugs in cancer therapy*, L.R. Kelland and N. Farrell, Humana Press, Totowa, NJ, 2001.

[2] V. Cobut, Y. Fongillo, J. P. Patau, T. Goulet, M.-J. Fraser and J.-P. Jay-Gerin, *Radiat. Phys. Chem.*, **51** (1998) 229.

[3] J. Kopyra, C. Koenig-Lehmann, I. Bald and E. Illenberger, *Angewandte Chemie Int. Ed.*, **48** (2009) 7904.

Precursor Design for Vapor-Phase Growth of Inorganic films

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The bottom-up synthesis of high quality inorganic nanostructures via liquid and gas phase methodologies is a well-established strategy. Various elemental and more complex compositions are produced via mixtures of precursor species or a single compound, the so called single-source precursor (SSP) concept.[1]

We present our strategies and findings to obtain volatile single source precursors. The limitations and benefits of specific ligand classes will be highlighted and differences in requirements for gas and liquid-phase processing will be pointed out. The control of molecularity and thermal decomposition behavior are important factors in designing the molecular entities for gas phase growth processes, such as low pressure chemical vapor deposition (LPCVD). The single source precursors discussed in this contribution are essentially homoleptic and heteroleptic metal-organic compounds which convert into the desired element semiconductor or oxide upon heat treatment. For instance, we synthesize volatile alkoxide molecules for the formation of oxide films and nanowires under LPCVD conditions. We will illustrate the influence of the precursor species by discussing the formation of Ge,[2] SnO₂ [3] and In₂O₃ films and nanostructures using simple thermally induced decomposition. In addition, we will show some examples of nanostructures prepared by this approach as well as a secondary decomposition of ligand species to achieve the intentional incorporation of elements in the thin film, which are not initially bonded to the metal center.

The contribution will address the general synthetic principles in precursor synthesis to avoid the formation of oligomeric species and influence of specific ligands will be discussed using specific examples.

[1] M. Veith, *J. Chem. Soc., Dalton Trans.* (2002) 2405.

[2] S. Barth, J. J. Boland, J.D. Holmes, *Nano Lett.* **11**, (2011), 1550.

[3] S. Barth, R. Jimenez-Diaz, J.Sama, J. D. Prades, I. Gracia, J. Santander, C. Cane and A. Romano-Rodriguez, *Chem. Commun.* **48**, (2012), 4734.

Electron-induced dissociative processes in FEBIP precursors and related moleculesJ. Fedor^{1,*}, R. Janečková¹, J. Kočišek¹, D. Kubala¹, O. May¹ and M. Allan¹

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We present cross sections for low-energy electron-induced processes in several molecules of technological relevance. The focus is put on scattering channels that lead to cleavage of the bonds and can thus contribute to the molecular decomposition in focused electron beam induced nanofabrication. Our experiments are performed on gas-phase molecules which collide with a beam of electrons with well-defined energy. We are mainly interested in electron energies up to 15 eV since cross sections in this range are often substantially enhanced by the occurrence of resonances.

A FEBIP precursor in which we have characterized all the electron scattering channels is Pt(PF₃)₄. We have shown that the dissociative electron attachment – a process leading to removal of one PF₃ ligand and creation of Pt(PF₃)₃⁻ ion – has a very large cross section of 20000 pm² [1]. It thus represents a very efficient bond-breaking reaction which can cause adverse effects in focused-beam nanofabrication. Similarly large cross sections have been found in a range of other FEBIP precursors [2]. Another process with relatively large cross section is electronic excitation of the target molecule [3]. Due to a small binding energy of ligands to the metal atom, it is reasonable to assume that the electronically excited states are dissociative and their population in the collision with an electron also leads to a bond cleavage. We compare the relative weights of the two bond-breaking processes by convoluting the measured cross sections with the distributions of secondary electrons in various materials.

Finally, we discuss the influence of bulk environment on the efficiency of above-mentioned processes. We do this by comparing our electron attachment cross sections obtained under the single-collision conditions with the values obtained in high-pressure electron mobility experiments. On the example of the c-C₄F₈O target molecule we show that a collisional stabilization of negative ions in the high-pressure environment leads to an order-of-magnitude increase of the attachment cross-sections.

[1] O. May, D. Kubala and M. Allan, *Phys. Chem. Chem. Phys.* **14** (2012)[2] S. Engmann, M. Stano, Š. Matejčík, O. Ingólfsson, *Angew. Chem. Int. Ed.* **50** (2011) 9475[3] M. Allan, *J. Chem. Phys.* **134** (2011) 204309

Electron-Initiated Proton Transfer in Molecular Systems

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Electron-initiated proton transfer has been studied using methods of quantum chemistry. The target molecular systems were nucleic acid bases and their complexes [1], amino acids [2], carboxylic and bicarboxylic acids [3], complexes of simple inorganic acids and bases [4]. The computational results were used to interpret anion photoelectron spectroscopy and electron energy loss spectroscopy results obtained in the groups of K.H. Bowen (Johns Hopkins University) and M. Allan (University of Fribourg).

[1] M. Gutowski, I. Dabkowska, J. Rak, S. Xu, J.M. Nilles, D. Radisic, K.H. Bowen, *Eur. Phys. J. D*, **20**, (2002) 43.

[2] M. Gutowski, I. Dabkowska, J. Rak, S. Xu, J.M. Nilles, D. Radisic, K.H. Bowen, *Eur. Phys. J. D*, **20**, (2002) 43. P. Skurski, J. Rak, J. Simons, M. Gutowski, *J. Am. Chem. Soc.*, **123**, (2001) 11073.

[3] Z.G. Keolopile, M. Gutowski, A. Buonaugurio, E. Collins, X. Zhang, J. Erb, T. Lectka, K.H. Bowen, M. Allan, in preparation.

[4] S.N. Eustis, D. Radisic, K. H. Bowen, R.A. Bachorz, M. Haranczyk, G.K. Schenter, and M. Gutowski, *Science*, **319**, (2008), 936.

Non-local manipulation of polyatomic molecules in the STM

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The elucidation of the response of small molecules to low energy electrons at surfaces is central to an understanding of FEBID. STM experiments allow the response of molecules to electron attachment to be studied at the single molecule level. I will discuss the manipulation of polyatomic molecules – notably chlorobenzene (C_6H_5Cl or PhCl) – anchored to a silicon surface, with a focus on new mechanisms [1] for single molecular manipulation via electron injection. Specifically I will report site-specific non-local atomic manipulation (leading to molecular desorption) of PhCl [2]: effectively this is 'remote control' of molecular manipulation. Whereas the STM tip is usually located above the molecule to be manipulated, in this process charge is injected remotely and travels through the crystal, mimicking the behaviour of a secondary electron generated in FEBID. We find that this non-local electron attachment mechanism is also thermally activated (barrier 0.4 eV) and suppressed by the proximity of the STM tip itself, both results explicable in terms of electron-driven excitation to an intermediate physisorbed state. Moreover we find that C-Cl bond *dissociation* in the molecule is also thermally activated [3], with an energy barrier of 0.8 ± 0.2 eV, which we correlate *thermal* excitation to the physisorbed (precursor) state of the molecule, where electron attachment occurs.

[1] P.A. Sloan and R.E. Palmer, *Nature* **434** 367 (2005).

[2] P.A. Sloan, S. Sakulsermsuk and R.E. Palmer, *Phys. Rev. Lett.* **105** 048301 (2010); *see also* "Electron 'submarines' help push atoms around", *E.S. Reich*, *New Scientist*, 31 July 2010, p. 11.

[3] S. Sakulsermsuk, P.A. Sloan and R.E. Palmer, *ACS Nano* **4** 7344 (2010); *see also* "Physisorbed molecules take the heat", *In Nano*, *ACS Nano* **4** 7040 (2010).

The spontelectric nature of films; implications for FEBID

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The characteristics of spontelectric films have recently been reviewed in [1]. On forming a film by gas phase deposition of a spontelectric material, a potential, typically of several volts, appears spontaneously on the surface of the film. This potential, linearly proportional to the thickness of the film, may be either positive or negative and gives rise to a corresponding spontelectric field in the film. The spontelectric field depends on both the nature of the material which is deposited and on the temperature at which the film is deposited, but not on the nature of the substrate surface upon the films is deposited. The spontelectric field for any substance is in general less for higher temperatures of deposition. At greater than a certain temperature of deposition, no spontelectric effect can be observed. Warming of a spontelectric film causes at first little change in the spontaneous potential on the surface of the film, but a critical temperature is reached at which the spontelectric effect decays abruptly. By analogy with ferromagnetism, this is referred to as the Curie point. The spontelectric effect is caused by partial dipole alignment in otherwise amorphous films.

Materials which show the spontelectric effect are very diverse and include species with dipole moments such as nitrous oxide, propane, toluene or CF_3Cl . Films of material may contain electric fields which can exceed 10^8 V/m. Spontelectric fields are created without any external stimulus, such as an applied electric field, hence the elided name 'spontelectric'.

As regards FEBID and spontelectrics, FEBID can be used to make 3D nanostructures for electronics. These will typically be structures of several tens of nanometers or more in thickness and may in general be spontelectric. In the FEBID technique, the topmost layer is FEBID processed, forming layers which accumulate underneath. Given that secondary electrons are the main agent, dissociative electron attachment (DEA) will cause fragmentation of the parent species in the familiar manner. The energy of secondary electrons will be modified if the material is spontelectric, which in turn will modify the DEA process.

[1] D. Field, O. Plekan, A. Cassidy, R. Balog, N.C. Jones, J. Dunger, *Int. Rev. Phys. Chem.*, **2013**, 32, 345

Abstracts

Posters

Low energy electron inelastic scattering on aromatic Self Assembled Monolayers

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Tailoring specific chemical functions of a solid surface represents a crucial issue in the perspective of future microelectronics devices and chemical or biological sensors. For building multi-functional chemical objects, one should achieve high selectivity in chemical modifications of targeted functional groups. For this purpose, low energy electrons (LEE, < 20 eV) impact on supported molecular films can induce selective molecular rearrangements by dissociative electron attachment (DEA) [1] and be used to drive surface chemistry. Electron incident energies associated to resonant attachment processes can be revealed by exploring LEE scattering on molecular films with High Resolution Electron Energy Loss Spectroscopy (HREELS).

Self Assembled Monolayers (SAMs) of thiols chemisorbed on gold are good candidates for the study of surface chemistry control by LEE irradiation. They are potential platforms for building chemical or biological sensors but chemical modifications targeted on spacer or tail chemical group may be wanted for this purpose [2, 3].

We present a study on aromatic model SAMs, i.e. Terphenyl-thiol ($C_6H_5-(C_6H_4)_2-SH$) SAMs deposited on gold, performed using HREELS. Extended energy loss spectra showing multiple vibrational excitations [4] and vibration excitation functions recorded by HREELS [5] allows probing the involved scattering mechanisms (dipolar, impact and resonant) in the 4-13 eV energy range. Furthermore, chemical transformations induced by electron impact will be discussed. LEE attachment irradiation regime [6] will be compared to the high energy regime (50 eV).

[1] I. Bald, J. Langer, P. Tegeder and O. Ingolfsson, *Int. J. Mass Spectrometry* **277**, (2008). 4

[2] e.g. A. Härtl et al., *Nature Materials* **3** (2004). 736 ; W. Yang et al., *Nature materials* **1** (2002). 253

[3] A. Turchanin, A. Tinazli, M. El-Desawy, H. Grossann, M. Schnietz, HH. Solak, R. Tampe and A. Götzhäuser, *Adv. Mater.* **20** (2008). 471

[4] P. Swiderek, H. Winterling, H. Ibach, *Chem. Phys. Lett.* **280** (1997). 556

[5] R. Azria, A. Lafosse, L. Amiaud, Sh. Michaelson, A. Hoffman, *Prog. Surf. Sci.* **86** (2011). 94

[6] L. Amiaud, J. Houplin, M. Bourdier, V. Humblot, R. Azria, C.-M. Pradier and A. Lafosse, *Phys. Chem. Chem. Phys.*, **16** (2014).1050

Novel approaches to study low-energy electron-induced reactions in complex systems

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Bond cleavages induced by low-energy electrons (LEE) are relevant for different fields ranging from nanolithography to DNA radiation damage. In this context it is increasingly important to study LEE-induced reactions in larger and more complex molecules and environments. For such studies novel experimental approaches must be pursued. We have developed a scheme to visualize single LEE-induced bond cleavages by atomic force microscopy (AFM) by using DNA nanostructures.[1,2] We use DNA origami nanostructures as a platform to immobilize specific chemical structures on predetermined positions. After irradiation with LEEs the intact modifications are identified by AFM.[1,2] With this technique we were able to quantify electron-induced bond breaking in different subunits of a modified DNA strand within a complex environment. More precisely, we determined the dissociation yield of a disulphide bond, a biotin subunit and a DNA oligonucleotide sequence within a DNA origami nanostructure. More detailed chemical information on the involved fragmentation products can be obtained from surface-enhanced Raman spectroscopy (SERS). Gold or silver nanoparticles are used to increase the Raman scattering efficiency. First results will be presented on electron-induced reactions studied by SERS.

[1] A. Keller, I. Bald, A. Rotaru, E. Cauet, K. V. Gothelf, F. Besenbacher, *ACS Nano* **6**, (2012) 4392.

[2] A. Keller, J. Kopyra, K. V. Gothelf, I. Bald, *New J. Phys.* **15**, (2013) 14.

[3] J. Prinz, B. Schreiber, L. Olejko, J. Oertel, J. Rackwitz, A. Keller, I. Bald, *J. Phys. Chem. Lett.* **4**, (2013) 4140.

The Cu(II) and Ag(I) with N,O donor ligands complexes as precursors of the hybrid layers

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Copper(II) and Ag(I) complexes were used to obtain the hybrid materials. The complexes with the Schiff bases obtained by the condensation reaction of (1*R*,2*R*)-(-)-cyclohexanediamine or 2-pyridinecarboxaldehyde (pen) with aldehydes e.g. pyrrole-2-carboxaldehyde, 2-hydroxyacetophenone, 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde and 2-hydroxyacetophenone were synthesized. The ligands and complexes were characterized by circular dichroism (CD), UV-VIS, fluorescence, IR and ¹H and ¹³C NMR (ligand and silver(I) complexes) spectra. The X-ray crystal of [Cu(II)((pen)(dtbhba))Cl]·0.083H₂O and [Cu(II)((pen)(dtbhba))(CH₃COO)] were obtained. The [Cu(II)((pen)(dtbhba))Cl]·0.083H₂O structure reveals porous nature with channels filled with water molecules running along c axis. The hybrid materials contained N,O donor ligands were obtained by the spin coating method using silicon, Si or glass as substrates. (Fig.1.) The rotation speeds were ranging from 600 to 3000 rpm in order to vary thickness and morphology of the layers.[1-2] Also the time of the spin coating process and the type of substrates activation were changed to influence the properties of the obtained materials. The N,O donor ligands and their copper and silver complexes were used as well. The morphology and composition of the layers were studied by scanning electron microscopy (SEM/EDS) and atomic force microscopy (AFM) and cathodoluminescence properties some of them were studied.

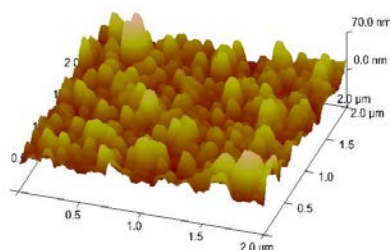


Fig. 1. AFM of [Cu(II)(pen(paH))Cl₂]/glass: 1000 rpm/min.

References:

- [1] M. Barwiolek, E. Szlyk, J. Lis and T Muzioł, *Dalton Trans.*, 40(41), (2011), 11012-11022.
- [2] M. Barwiolek, E. Szlyk, A. Surdykowski and A. Wojtczak, *Dalton Trans.*, 42, (2013), 11476-11487.

Can silicon chemistry advance FEBID?

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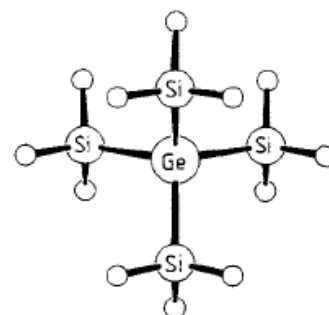
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An ideal precursor metal complex in focused electron beam induced deposition (FEBID) fragments completely under electron impact to yield the bare metal while its ligands are converted into volatile and non-reactive products. Unfortunately, this is often not the case. In particular, carbon containing ligands tend to crosslink under electron exposure so that the desired metal is embedded in a carbon matrix having most likely a graphite-type structure. This may deteriorate deposit properties such as the electrical conductivity [1]. In contrast, silicon crystallizes in diamond-type lattices highly relevant for semiconductors, but not in graphite-type structures. Using silyl groups as ligands may thus lead to deposition a more interesting material even if the ligands can not be fully removed. However, silicon compounds can have low cross sections for dissociative electron attachment (DEA) [2], a process which is particularly efficient at near-thermal electron energies but often leads to a very incomplete fragmentation. If this process is inefficient so that fragmentation proceeds predominantly via electron impact ionization channels that may yield a much higher degree of fragmentation [3], purer deposits may also be anticipated.

Based on these arguments, we thus propose to investigate the fragmentation behaviour of compounds such as $\text{Ge}(\text{SiH}_3)_4$ [4] in comparison with its alkyl analogue $\text{Ge}(\text{CH}_3)_4$ and develop synthetic approaches to similar compounds $\text{M}(\text{SiH}_3)_n$ containing other types of metal centres.



- [1] I. Utke, P. Hoffmann, J. Melngailis, *J. Vac. Sci. Technol. B* **26** (4), 1197 (2008).
 [2] I. Ipolyi, E. Burean, T. Hamann, M. Cingel, S. Matejcik, P. Swiderek, *Int. J. Mass Spectrom.* **282**, 133 (2009).
 [3] S. Engmann, M. Stano, S. Matejčík, O. Ingólfsson, *Angew. Chem. Int. Ed.* **50**, 9475 (2011).
 [4] T. Lobreyer, H. Oberhammer, W. Sundermeyer, *Angew. Chem. Int. Ed.* **32**, 586 (1993).

Investigation and application prospects of complementary studies in electron beam and tunneling electron induced precursor decomposition

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The electron beam assisted growth of Mo nanoparticles using Mo(CO)₆ as precursor was studied in our laboratories from several different aspects last years [1-3]. The results of these investigations on STM-CVD and EBI-CVD processes led us to reason the complementary features of the methodical and experimental techniques applied therein (XPS, EXAFS, LEED, TDS, STM, STS). Concerning of the initial reaction steps toward the complete electron induced dissociation of carbonyls, it was shown by STM-CVD that partially and uniformly dissociated ordered layers can be formed after the substantial change of the original bond to the surface [3]. This locally (in the STM scan region) induced effect is probably appears also on large scale in an EBI-CVD process, but it is more difficult to prove. At the same time, the metal cluster formation following complete carbonyl decomposition can be clearly detected by both methods (STM-CVD and FEBID) and the efficiency of these procedures can be systematically compared. In this way, there is a chance to obtain a more detailed picture on the particle formation, its chemical composition and the side effects accompanying electron beam assisted growth. Speculating one step forward, from the point of view of applications, the STM-CVD and FEBID can also be used as complimentary sequential procedures. Regarding that the ultimate resolution of high quality EBID is around 5 nm and for the STM-CVD this limit is somewhere around 1 nm, accordingly, a sample on which nanopatterns were previously formed by FEBID can also be used for a further development of the nanopatterns by appropriate STM-CVD processes.

References

- [1] Z. Majzik, N. Balázs, L. Robin, M. Petukhov, B. Domenichini, S. Bourgeois and A. Berkó: Tunneling Induced Decomposition of Mo(CO)₆ onto TiO₂(110) surface, *Vacuum* **86** (2012) 623-626.
- [2] M. Petukhov, P. Krüger, B. Domenichini, S. Bourgeois: Mo(CO)₆ dissociation on Cu(111) stimulated by scanning tunneling microscope, *Surface Science* **617** (2013) 10-14.
- [3] P. Paufert, E. Fonda, Z. Li, B. Domenichini, S. Bourgeois: Watching adsorption and electron beam induced deposition on the model system Mo(CO)₆/Cu(111) by X-ray absorption and photoemission spectroscopies, *Applied Surface Science* **284** (2013) 248-253.

New Instruments dedicated to Focused Electron Beam Induced Deposition

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Abstract

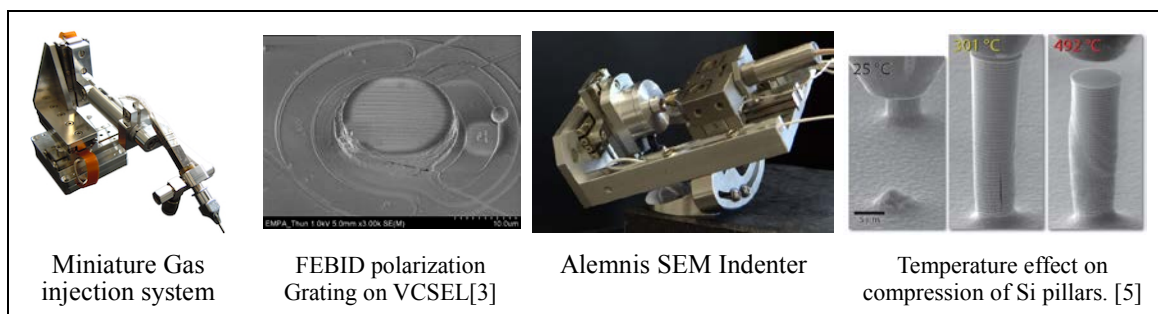
Alemnis is a SME based in Thun, Switzerland. Alemnis is specialized in developing, manufacturing and integrating customized instruments and tools compatible with scanning electron microscopes (SEM), focused electron/ion beam induced deposition (FIB), light microscopes or Synchrotron's beam lines. The primary applications are within mechanical characterization in all kinds of micro- and nano devices or components.

In the frame of several EU and national projects, Alemnis has developed in close cooperation with EMPA, a miniaturized, modular gas injection system (GIS) which can supply metalorganic or other molecule precursors for local chemical reactions inside the vacuum chambers of scanning electron microscopes and focused ion beam instruments [1, 2, 3].

Alemnis is also well known for its SEM Indenters used for studying material and mechanical properties at micro and nano-scales [4, 5].

CELINA cost action is an interesting opportunity for Alemnis to understand what innovation in scientific instruments is needed to push further the limit of in EBID discovery.

We are confident Alemnis will contribute significantly to EBID research by providing the adequate instruments for the fabrication (GIS and agile positioning systems) and their mechanical characterization of EBID nanostructures (SEM Indenter).



- [1] M. S. Gabureac, L. Bernau and I. Utke, "Nanosynthesis of Tunable Composite Materials by Room-Temperature Pulsed Focused Electron Beam Induced Chemical Vapour Deposition", *Journal of Nanoscience and Nanotechnology* Vol. 11, 7982–7987, 2011.
- [2] M.G. Jenke, D. Lerose, I. Utke et al., "Toward Local Growth of Individual Nanowires on Three-Dimensional Microstructures by Using a Minimally Invasive Catalyst Templating Method", *Nano Lett.* 11 (2011) 4213–4217.
- [3] I. Utke, M.G. Jenke et al., "Polarization stabilization of vertical cavity surface emitting lasers by minimally-invasive focused electron beam triggered chemistry", *Nanoscale* 3(7) (2011) 2718-2722.
- [4] Adusumalli, R.B.; Koodakal, R.R.; Schwaller, P.; Zimmermann, T.; Michler, J., "In situ SEM micro-indentation of single wood pulp fibres in transverse direction", *J. Electron. Microsc.*, 2010, 59, 5, 345-349, Oxford University Press; JEM
- [5] J.M. Wheeler, J.-M. Breguet, R. Rabe, D. Frey, R. Raghavan and J. Michler, "Instrumentation for displacement controlled, cyclic, elevated temperature, nanomechanical testing", *Micromechanical Testing In Materials Research And Development IV*, Olhão, Portugal, October 6-11, 2013.

Electron Beam Induced Processing as a lithographic tool for the generation of iron nanostructures on Si(100), silicon oxide and silicon nitride

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Electron beam induced processing techniques use a focused electron beam, for example from a scanning electron microscope (SEM), to fabricate nanostructures with lithographic control. One of these techniques is electron beam induced deposition (EBID) in which a highly focused electron beam locally decomposes adsorbed molecules that leave a deposit of nonvolatile fragments [1,2]. Metallic nanostructures are mostly generated from organometallic precursors in a high vacuum (HV) environment. By employing iron pentacarbonyl $\text{Fe}(\text{CO})_5$ as a precursor and EBID under UHV conditions we are able to produce very clean iron nanostructures on Si(100) with a high metal content (>95%) and with dimensions around 10 nm [3]. A second technique is electron beam induced surface activation (EBISA): In a first step, the surface is irradiated and thereby locally activated with a focused electron beam, and in a second step, it is exposed to $\text{Fe}(\text{CO})_5$. The gas dissociates at the active sites to form initial small nuclei which grow autocatalytically at room temperature until the precursor supply is stopped. We have successfully employed this approach to generate iron nanostructures on commercial 300 nm SiO_x films on Si(100) [4], on ultra-thin SiO_x films (thickness of around 0.5 nm) on Si(100) prepared *in situ* under UHV conditions [5] and on silicon nitride, and on thin membranes of 50 and 200 nm thick silicon nitride layers on a Si crystal [6]. Autocatalytic growth of EBID Fe deposits upon prolonged precursor dosage has also been studied on silicon nitride and Si(100) covered by a native oxide. A comparison of the previously obtained results on the different substrates will be presented including a discussion of the nature of the "activated" sites in EBISA, the influence of possible charging effects, and the impact of proximity effects by back scattered electrons (BSE).

- [1] I. Utke, P. Hoffman, J. Melngailis, *J. Vac. Sci. Technol. B* **26**, (2008) 1197.
- [2] W. F. van Dorp and C. W Hagen, *J. Appl. Phys.* **104**, (2008) 081301.
- [3] T. Lukaszcyk, M. Schirmer, H.P. Steinrück, H. Marbach, *Small*, **4** (2008) 841.
- [4] M.M. Walz, M. Schirmer, F. Vollnhals, H.P. Steinrück, T. Lukaszcyk and H. Marbach, *Angew. Chem. Int. Ed.* **49**, (2010) 4669.
- [5] M.M. Walz, F. Vollnhals, M. Schirmer, H.P. Steinrück and H. Marbach, *Phys. Chem. Chem. Phys.* **13**, (2011) 17333
- [6] M.M. Walz, F. Vollnhals, M. Schirmer, H.P. Steinrück and H. Marbach, *J. Phys. D: Appl. Phys.* **45**, (2012) 225306

Search for Resonances in Electron Scattering by Small and Medium-Sized Molecules by Joint Theoretical and Experimental Studies

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The purpose of this poster is to show our partners in the CELINA project a recent progress made in determination of resonances in electron scattering. As the resonances are clear-cut in plots for vibrationally inelastic scattering more than for elastic scattering, we concentrated primarily on the former. For our poster we selected material from our recent work on cyclopropane [1,2], diacetylene [3] and benzene [4]. As an example we show in Figure 1 identification of the A_2'' resonance for cyclopropane. The largest molecule treated so far was benzene. We are working now on upgrade of our program to make calculations feasible for molecules that are larger in size. It is our objective to do next calculations on molecules that could represent models for precursors and reaction intermediates in intended FEBID experiments.

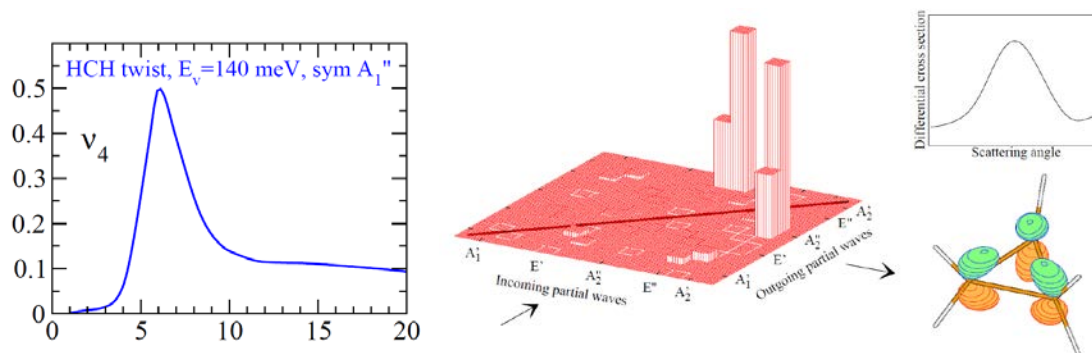


Figure 1. Identification of symmetry of A_2'' resonance for cyclopropane. The left panel shows energy dependence of inelastic cross section of HCH twist mode excitation. At the poster we explain the meaning of the right side of the cartoon. It shows the dominant partial waves, their symmetries, angular shape of the cross section and the corresponding virtual molecular orbital.

[1] R. Čurík, P. Čársky and M. Allan, *Phys.Rev A*. **86** (2012) 062709.

[2] R. Čurík, P. Čársky and M. Allan, *J. Chem. Phys.*, to be published.

[3] M. Allan, R. Čurík, I. Paidarová and P. Čársky, *J. Phy., Chem. A*, to be published.

[4] to be published.

Growth optimization of high-purity and high-aspect-ratio three-dimensional cobalt structures by FEBID

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Focused-electron-beam induced deposition of three-dimensional (3D) cobalt nanowires with high metallic content (over 90 % at.) and narrow width (≈ 80 nm) is reported. An appropriate scanning strategy is necessary in order to achieve high cobalt content and aspect ratio. The influence of the precursor flux, refresh time and dwell time in the metallic content and structure height is discussed. Morphology defects appear caused by heating effects, although they can be avoided using appropriate growth conditions. The structural and magnetic characterization of these 3D nanowires prove their functionality [1, 2].

[1] Fernández-Pacheco, A.; Serrano-Ramón, L.; Michalik, J.; Ibarra, M. R.; De Teresa, J. M.; O' Brien, L.; Petit, D.; Lee, J.; Cowburn, R. P. Three dimensional magnetic nanowires grown by focused electron-beam induced deposition. *Sci. Rep.* **2013**, 3, 1492.

[2] Serrano-Ramón, L et al., manuscript in preparation

Combining Focused electron beam induced processing with self-assembled functional molecules

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Electron Beam Induced Deposition (EBID) has attracted increasing interest in the last few decades for the fabrication of nanosized structures. In our investigation of EBID with iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) on an $\text{Ag}(111)$ surface, we observed decomposition and autocatalytic growth of iron structures on the whole surface, even without electron irradiation. Herein, we show that the initial decomposition can be inhibited by a preadsorbed layer of porphyrin molecules on $\text{Ag}(111)$. On the corresponding “organic interface” well-defined Fe nanostructures can be produced via EBID with $\text{Fe}(\text{CO})_5$. In analogy to the recently introduced electron beam induced surface activation (EBISA) process [1], we can also use the electron beam to locally irradiate the porphyrin layer with the electron beam and thereby activate selected areas for the catalytic growth of $\text{Fe}(\text{CO})_5$. Thus, we can apply two different fabrication routes for iron deposits on $\text{Ag}(111)$. In both, the first step is the deposition of the porphyrin layer. Thereafter, we can either perform the conventional EBID process or we can use the electron beam for the local activation. In this contribution, we demonstrate that by focused electron beam processing (FEBIP) one can chemically activate ultrathin organic layers, here 2H-Tetraphenylporphyrin (2HTPP), on $\text{Ag}(111)$, such that $\text{Fe}(\text{CO})_5$ is decomposed at these regions [2].

Furthermore, we investigate the feasibility of FEBIP to locally modify surfaces, such that they act as templates for the directed adsorption of functional molecules. First, the adsorption behavior of 2HTPP on $\text{Cu}(111)$ and $\text{Rh}(110)$ with and without oxygen was studied. Second, with the aim to locally remove oxygen by electron beam induced oxygen desorption, the influence of irradiating the surface with an electron beam was investigated.

All studies were performed by a combination of Scanning Electron Microscopy (SEM), Scanning Tunneling Microscopy (STM), Auger Electron Spectroscopy (AES) and Scanning Auger Microscopy (SAM).

[1] M.-M. Walz, M. Schirmer, F. Vollnhals, T. Lukasczyk, H.-P. Steinrück and H. Marbach, *Angew. Chem. Int. Ed.* **49** (2010), 4669

[2] F. Vollnhals, P. Wintrich, M.-M. Walz, H.P. Steinrück and H. Marbach, *Appl. Phys. Lett.* **100**, (2008). 053118

Dissociative electron attachment to $W(CO)_6$

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Metal carbonyl complexes have been used in the field of plasma technology for metal deposition and in the case of tungsten layer, tungsten hexacarbonyl – $W(CO)_6$ is widely used in Electron Beam Induced Deposition (EBID), and Ion Beam Induced Deposition (IBID). In both techniques, high energy electron or ion beams are used to promote metal deposition into a solid substrate. However, low energy electrons are formed as secondary species, and so, those contribute for deterioration of spatial resolution when using such techniques. These secondary electrons have energy distribution below 20 eV where dissociative electron attachment (DEA) processes plays an important role as far as decomposition pathways are concerned. In this communication we present recent DEA studies on $W(CO)_6$ in the gas phase. The energetics and reaction dynamics of the DEA reaction, between 0 and 14 eV, have been studied for this molecule. The experiments were performed using a double focusing mass spectrometer with an electron energy resolution of about 1 eV (FWHM) as well as using a Trochoidal Electron Monochromator (TEM) with an electron energy resolution of about 60 meV (FWHM). The experimental results show efficient cleavage of one or more CO groups below 10 eV.[1]

[1] K. Wnorowski, M. Stano, C. Matias, S. Denifl, W. Barszczewska, Š. Matejčík, *Rapid Comm. Mass Spectrom.*, **26**, (2012), 2093

Clustering and condensation effects in the electron scattering cross sections from water molecules

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Clustering effects in the differential and integral electron scattering cross sections have been investigated by calculating their magnitudes for different water cluster configurations: specifically for the dimer, trimer and tetramer. By assuming that condensation effects can be described in terms of modifications to the single molecule electron scattering cross sections, induced by the surrounding molecules, effective data for liquid water is also provided. Comparison with previous calculations in liquid water has been carried out through the inelastic mean free path, i. e. the mean length between successive inelastic collisions. Although a satisfactory agreement for high energies, above 100 eV, has been found, for lower energies some discrepancies remain and so will be the subject of further investigation. As an example of modelling electron interactions in soft matter, the present set of data has been employed to simulate single electron tracks in liquid water. This was achieved using our Low Energy Particle Track Simulation (LEPTS) code [1].

[1] F. Blanco, A. Muñoz, D. Almeida, F. Ferreira da Silva, P. Limão-Vieira, M. C. Fuss, A. G. Sanz, G. García, *Eur. Phys. J. D* **67** (2013) 199.

A Cobalt Layer Deposition Study: Dicobalttetrahedranes as Convenient MOCVD Precursor Systems

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We herein describe the straightforward synthesis of cobalt precursors of general type $\text{Co}_2(\text{CO})_6(\eta^2\text{-RC}\equiv\text{CR}')$ ($\text{R} = \text{R}' = \text{SiMe}_3, \text{C}_2\text{H}_5$; $\text{R} = \text{H}, \text{R}' = \text{SiMe}_3, {}^n\text{C}_4\text{H}_9, {}^n\text{C}_5\text{H}_{11}, {}^n\text{C}_6\text{H}_{13}, {}^n\text{C}_7\text{H}_{15}$; $\text{R} = {}^n\text{C}_3\text{H}_7, \text{R}' = \text{SiMe}_3, \text{CH}_3$) and their use as straightforward CVD precursors for thin cobalt film deposition. The substituents R and R' allow to decrease the melting points and to increase the vapor pressures of the appropriate dicobalttetrahedranes.^[1] The thermal behavior of $\text{Co}_2(\text{CO})_6(\eta^2\text{-HC}\equiv\text{CSiMe}_3)$ is discussed in detail. Furthermore, vapor pressure measurements were carried out to get first information of the volatility of the newly prepared dicobalttetrahedranes to compare them to well-known MOCVD precursors, e.g. cobaltocene and dicobaltoctacarbonyl^[2,3].

Cobalt layers of high quality were formed by the MOCVD process using a cold-wall reactor applying the synthesized dicobalttetrahedranes in the temperature range of 250 - 380 °C. As carrier gas nitrogen was utilized without application of any reactive gas. The conformal and dense cobalt layers show cobalt content of up to 97 mol%.

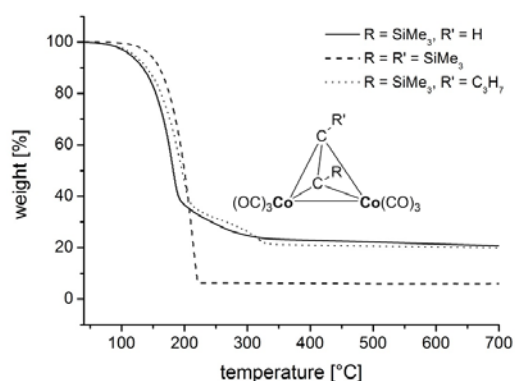


Fig. 1 TG traces of SiMe_3 -substituted dicobalttetrahedranes $\text{Co}_2(\text{CO})_6(\eta^2\text{-RC}\equiv\text{CR}')$.^[4]

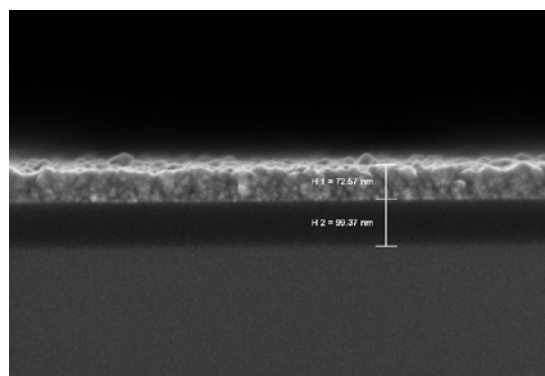


Fig. 2 Cobalt layer grown from $\text{Co}_2(\text{CO})_6(\eta^2\text{-HC}\equiv\text{CSiMe}_3)$.^[5]

[1] A. Tuchscherer, C. Georgi, N. Roth, D. Schaarschmidt, T. Rüffer, T. Wächtler, S.E. Schulz, S. Oswald, T. Geßner, H. Lang, *Eur. J. Inorg. Chem.*, **30** (2012). [2] M. T. Vieyra-Eusebio, A. Rojas, *J. Chem. Eng. Data*, **56**, (2011). [3] M. L. Garner, D. Chandra, K. H. Lau, *J. Phase Equilib.*, **16**, (1995). [4] C. Georgi, A. Hildebrandt, T. Waechter, S. E. Schulz, T. Gessner, H. Lang, *Chem. Mater.*, submitted. [5] C. Georgi, A. Hildebrandt, A. Tuchscherer, S. Oswald, H. Lang, *Z. Anorg. Allg. Chem.*, **639**, (2013).

Multi-purpose Multi-beam SEM with 196 beams

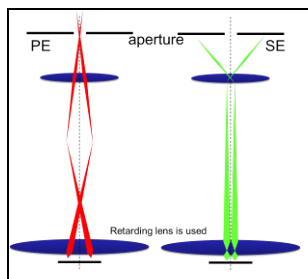
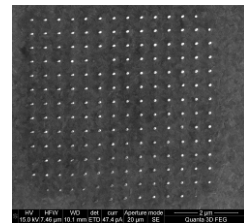
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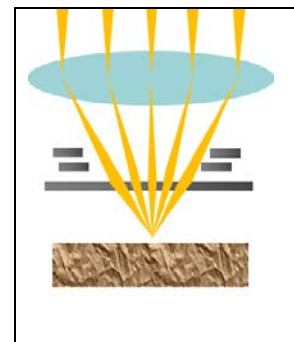
Electron beam systems, such as electron microscopes or electron beam lithography machines, are inherently slow because the imaging or patterning is a serial process. The ongoing miniaturization in electronic devices, though, requires high-resolution imaging and high-resolution patterning, at high throughput. The solution for that is to use more beams in parallel. We developed a multi-beam Scanning Electron Microscope (MBSEM) with 196 beams, each beam having the same probe size and probe current as a regular single beam SEM [1,2]. This system has a threefold purpose:

1. By adding a gas injection system it can be used for multi electron beam induced deposition, and 196 pixels can be deposited simultaneously. The SEM image shows an array of dots deposited at 20 keV, using the MeCpPtMe₃ precursor, in a single 20 s exposure [3].



2. By adding a retarding electrostatic lens below the magnetic objective lens the secondary electrons generated by each primary beam are accelerated towards an in-lens detection plane with a narrowed opening angle. Neighboring secondary electron spots, originating from neighboring primary electron beams, are well separated at the detector plane. High-throughput multi-beam imaging is achieved this way.

3. By adding an electrostatic macro lense and a micro-fabricated lens array below the magnetic objective lens, the 196 beams can be focused in a medium resolution spot of 50 nm, with 200 nA of current, at 500 V landing energy. This way the MBSEM can be used as a high-current fast wafer inspection SEM.



We will discuss the different designs and present initial results.

[1] A. Mohammadi-Gheidari, C.W. Hagen and P. Kruit, *Journal of Vacuum Science & Technology B* **28**, C6G5 (2010)

[2] A. Mohammadi-Gheidari and P. Kruit, *Nuclear Instruments and Methods in Physics Research Section A* **645**, 60 (2011)

[3] P.C. Post, A. Mohammadi-Gheidari, C.W. Hagen and P. Kruit, (2011). *Journal of Vacuum Science & Technology B* **29**, 06F310 (2011)

[4] T. Ichimura, Y. Ren and P. Kruit, *Microelectronic Engineering* **113**, 109–113 (2014)

Size and shape control of sub-20 nm structures fabricated by Electron Beam Induced Deposition

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Electron Beam Induced Deposition (EBID) is an attractive direct write technique for high resolution (sub-20 nm) patterning [1]. However, achieving control over the dimensions of the structures fabricated by EBID is still a challenge because, although the primary electrons are guided to write the specified pattern, there is no control over processes initiated by the secondary and backscattered electrons. In addition, a number of parameters are involved in the deposition process, many of which are not well known or vary between experiments. For example, the manner and rate of growth of structures depends on whether the experimental conditions are those of the precursor-limited regime or the electron current-limited regime. This in turn depends on parameters such as the precursor gas flux and precursor surface diffusion. We aim to characterize the EBID process in terms of these parameters.

Lines were patterned by EBID from the commonly used organometallic precursor MeCpPtMe₃ and the width and line edge roughness (LER) were analyzed using a recently developed technique [2] (Fig.1). The lines have an average width of 13.7 nm and an average LER of 4.5 nm (1 σ). Serial and parallel patterning modes were applied and the results compared, as well as single pass and multiple pass patterning. First results of this quantitative analysis will be presented and further experiments towards achieving shape control will be discussed.

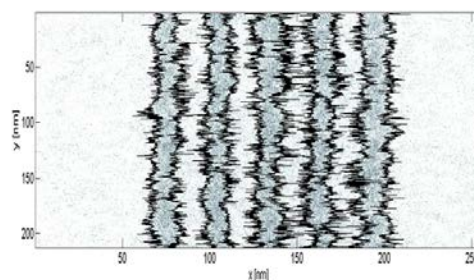


Fig.1 Contrast enhanced secondary electron image of five EBID lines. The black lines indicate the edges that were fitted using the algorithm described in [2].

References:

- [1] W. F. van Dorp, B. van Someren, C. W. Hagen, P. Kruit, *Nano Letters* **5** (2005) 1303-1307
- [2] T. Verduin, P. Kruit, C.W. Hagen, to be published in SPIE Advanced Lithography Proceedings 2014

Biofunctionalizing Surfaces by Resist-free Electron Beam Patterning

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Biofunctionalized nano scale arrays are an important tool in the study of several biological processes, especially to monitor interactions between single molecules. A flexible technique to biofunctionalize surface is described by Schlapak et al [1]. Carbon containing nanopatterns ($100 \times 100 \text{ nm}^2$) were created on a glass/ITO (17 nm) substrate coated with PEG silane with the help of a focused electron beam in a Scanning Electron Microscope (SEM). Upon incubating this sample in a solution of IgG-Cy3 followed by rinsing, the electron beam-patterned islands were observed to fluoresce with a high contrast (> 1000) with respect to the surrounding PEG silane layer. Further, upon increasing the electron dose per island, an increase in the fluorescence intensity was observed which is attributed to increased binding (physisorption) of the biomolecules to the structure. Although an increase in electron dose (from 0 to 200 C/m^2) is seen to cause an increase in the lateral dimensions as well as the height of the structure, the fluorescence analysis in combination with AFM measurements of the height led them to conclude that the binding depends largely on the height of the structure. This is a versatile method applicable to a variety of proteins, enabling easy tuning of the local biomolecule density. Further, since the binding conforms to the shape of the nanopatterns, the resolution of such a functionalization approach could in principle approach a few nanometers [2].

We aim to study in more detail the processes taking place, in particular, the electron dose dependence of the fluorescence intensity, with the ultimate goal of achieving high resolution (sub 10 nm) biofunctionalized patterns. The sample was patterned in a Nova Nano 650 Dual Beam system at 5 keV and 24 pA current. The pattern consists of an array of squares ($1 \mu\text{m} \times 1 \mu\text{m}$) written with increasing dose from 50 C/m^2 to 1800 C/m^2 . After incubation in a solution of IgG-Alexa 488 the sample was examined in a fluorescence microscope, with surprising results. The structures themselves are observed not to fluoresce. Instead, the fluorescence appears to come from the edges of the structures (see figure), with higher dose areas yielding greater intensity as in [1]. However, regions of the sample that were not patterned but imaged shortly in the SEM, and therefore received a low electron dose, are seen to fluoresce completely. This suggests that the binding is possibly electron dose dependent and results from chemical modification of the PEG silane layer and/or electron beam induced deposition (EBID) from hydrocarbons in the SEM chamber due to the secondary electrons generated in the process. This dose dependence was studied in more detail and the results will be presented.

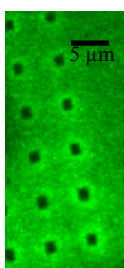


Figure: Fluorescence image demonstrating fluorescence from the sides of the nano patterns (black squares)

- [1] R. Schlapak, J. Danzberger, T. Haselgrubler, P. Hinterdorfer, F. Schaffler, S. Howorka, *Nano Letters* **12** (2012) 1983-1989
 [2] W. F. van Dorp, B. van Someren, C. W. Hagen, P. Kruit, *Nano Letters* **5** (2005) 1303-1307

Nano-granular FEBID structures for dielectric sensor applications

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It is thin films and, in particular, their interfaces that define the electronic functionality of devices. The ferroelectric (FE) state represents an important example in this regard, since the ability to switch the electric polarization by an electric field is the basic property needed in ferroelectric random access memories or field effect transistors [1]. For both, applied and basic research, the ability to tune the paraelectric (PE) to FE transition to a large degree is very attractive. How can this tuning be accomplished? Two mechanisms are particularly suitable for thin film structures, namely clamping effects and interfacial charge transfer. Clamping effects occur, if a thin film strongly adheres to a bulk substrate and follows its elastic response, e.g., thermal expansion effects in the consequence of temperature changes. Interfacial charge transfer is governed by the interfacial electronic states which form when the thin film is deposited on a substrate surface or as part of a multi-component heterostructure. An important question in analyzing the FE state or, more general, the dielectric properties of a layered structure, is: How can the influence of clamping and charge transfer be monitored, ideally in a way that does not interfere with the dielectric state itself? We show that strong modulations in the Coulomb blockade effect in a nano-granular metal occur, if this is in close proximity to a FE thin film. These modulations lead to easily detectable changes in the electrical conductance which thus becomes a minimally invasive probe of the FE state, its temperature and electric field dependence, as well as its dynamic properties. We demonstrate the monitoring effect for a bilayer thin film structure consisting of the organic ferroelectric [tetrathiafulvalene]^{+δ}[p-chloranil]^{-δ} (TTF-CA) and a Pt-based nano-granular metal (Pt(C)) prepared by focused electron beam induced deposition (FEBID). TTF-CA is an organic CTS that shows a valence instability, also called neutral-ionic phase transition, at about 84K which drives the system from a PE to a FE state [2]. Nano-granular Pt(C) consists of fcc-Pt crystallites of 2-3 nm diameter embedded in an amorphous carbon matrix. Pt(C) grown by FEBID has shown to provide a model system for studying charge transport effects in nano-granular metals with tunable inter-grain coupling strength [3]. In a nano-granular metal charge transport occurs via inelastic tunneling between the metallic grains. Due to the very small size of the individual Pt crystallites, this charge transport is governed by the charging energy E_C associated with each tunnel event (Coulomb blockade effect). It is this charging energy which is very sensitive to the dielectric properties of neighboring dielectric layers. As a consequence, the onset of the FE state associated with a pronounced increase of the dielectric constant $\epsilon_r(T)$ of TTF-CA can be detected as a very pronounced change in the temperature-dependent conductance of the nano-granular metal. We provide a theoretical framework to understand the observed conductance changes and provide exemplary model calculations that take the anisotropy of the dielectric anomaly at the PE/FE phase transition into account. Our data suggest that this approach is very suitable for observing dynamical effects close to the PE/FE phase transition, such as fluctuations in the dielectric constants due to the coexistence of PE and FE domains or the movement of FE domains. Because of the FEBID fabrication method of the nano-granular metal, our approach provides excellent down-scaling capabilities. Monitoring the FE state on the lateral scale of individual growth domains (a few 100 nm) can therefore be envisioned.

[1] M. Dawber, K. M. Rabe and J. F. Scott, *Rev. Mod. Phys.* 77, (2005). 1083

[2] J.B. Torrance, J.E. Vazquez, J. J. Mayerle and V. Y. Lee, *Phys. Rev. Lett.* 46, (1981). 253 [3] R. Sachser, F. Porrati, Ch. H. Schwalb and M. Huth, *Phys. Rev. Lett.* 107, (2011). 206803

Vibrational fingerprints of tungsten and cobalt based molecules adsorbed on silica surfaces

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Tungsten and cobalt carbonyls adsorbed on a substrate are typical starting points for the electron beam induced deposition of tungsten or cobalt based metallic nanostructures. We employ first principles molecular dynamics simulations to investigate the dynamics and vibrational spectra of $W(CO)_6$ and $W(CO)_5$ as well as $Co_2(CO)_8$ and $Co(CO)_4$ precursor molecules on fully and partially hydroxylated silica SiO_2 surfaces [1,2,3]. Such surfaces resemble the initial conditions of electron beam induced growth processes. We find that both $W(CO)_6$ and $Co_2(CO)_8$ are stable at room temperature and quite mobile on a silica surface saturated with hydroxyl groups (OH), moving up to half an Angstrom per picosecond. In contrast, chemisorbed $W(CO)_5$ or $Co(CO)_4$ ions at room temperature do not change their binding site. These results contribute to gaining fundamental insight into how the molecules behave in the simulated time window of 20 ps and our determined vibrational spectra of all species provide signatures for experimentally distinguishing the form in which precursors cover a substrate.

[1] K. Muthukumar, I. Opahle, J. Shen, H. O. Jeschke, and R. Valentí, *Phys. Rev. B* **84** (2011), 205442

[2] K. Muthukumar, H. O. Jeschke, R. Valentí, E. Begun, J. Schwenk, F. Porrati, and M. Huth, *Phys. J. Nanotechnol.* **3** (2012), 546

[3] K. Muthukumar, R. Valentí, and H. O. Jeschke, arXiv:1306.2567 (unpublished).

Cobalt carbonyls as a candidate for producing metal nanoparticles on oxide nanostructures

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Well-characterized cobalt either in metallic or ionic states play a very important role in several catalytic processes. Especially the steam reforming of ethanol and Fisher-Tropsch synthesis requires controlled size cobalt nanoparticles on oxide support. The elegant ways of producing metal nanoparticles are photo-induced and electron-assisted metal-CO bond cleavage in carbonyl substrate. The main advantage of these processes is that no high temperature calcination is necessary, therefore, adverse effects frequently occurring during more conventional metal deposition processes like sintering of Co nanoclusters and destruction of the support structure can be avoided.

Different structures of Co-carbonyls ($\text{Co}_2(\text{CO})_8$, $\text{Co}_4(\text{CO})_{12}$) and NO substituted carbonyls (such as $\text{Co}(\text{CO})_3\text{NO}$) are candidates as precursor molecules. They have different physical-chemical properties. The octacarbonyl was tested in UHV systems for producing metal deposits on oxides by EBID. Unlike the use of iron or molybdenum carbonyls, several technical problems arise during UHV handling. However, in the course of low-temperature decomposition surface science experiments on titania nanowires with octacarbonyl provided several important observations for further investigations.

Cobalt carbonyl on protonated titanate nanowires was characterized by FT-IR spectroscopy, XPS, XRD and HRTEM. In solid state the structure of $\text{Co}_2(\text{CO})_8$ is of C_{2v} point group symmetry involving a pair of bridging group. The IR spectrum of adsorbed carbonyl at 323 K is very similar to that observed in heptane solution and it is close to that obtained on porous silica. Two strong bands were observed at 1986 and 2036 cm^{-1} and weak and broad bands were detected at 1928 and 1872 cm^{-1} , respectively. The characteristic bands disappeared at about 623 K indicating the decomposition of the $\text{Co}_2(\text{CO})_8$. This process results in the formation of nanosized-dispersed Co particles complexed with oxygen vacancies. The average size was found to be mostly between 2 and 6 nm by HRTEM and XRD.

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The study of dissociative electron attachment to Iron pentacarbonyl molecule

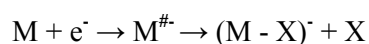
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Organometallic compounds are recently subject of interest in many areas of research, mainly in nanotechnology. Their use is primarily applied in the FEBID – Focused Electron Beam Ion Deposition technology. From this reason it is necessary to investigate processes occurring at electron – molecular interactions. In this work we are presenting the study of processes emerging at low electron energy, electron attachment (EA) and the corresponding dissociative electron attachment (DEA), which can be written as



where M and X represent the investigated molecule neutral fragment respectively. In this study we were interested in investigation of processes occurring on Iron pentacarbonyl (Fe(CO)₅) molecule, which is in FEBID technology commonly used. Research is carried out in the laboratory of crossed electron beams at the Comenius University in Bratislava. Experimental setup of the crossed electron and molecular beams apparatus is equipped with trochoidal electron monochromator, which allows creation of monoenergetic electron beam with resolution below 100 meV, but around 200 meV in the present experiment. Molecular source enables to study gas phase, liquid as well as solid state samples, which are introduced into the high vacuum through a small capillary. Ions produced by DEA are then extracted from the reaction region by a weak electric field through a quadrupole mass analyzer into the detector.

DEA to Iron pentacarbonyl leads to create negative ions via dissociation of one or more CO ligands. Recently observed ions Fe(CO)₄⁻ and Fe(CO)₃⁻ are produced by single particle resonances at energies near zero and 1.2 eV, as well. Ions Fe(CO)₂⁻, Fe(CO)⁻ and Fe⁻ are produced by core excited resonances in the region between 3 – 5.5 eV, 5 – 11 eV and near 9 eV, as well. Cross section of dissociative reaction decreases with the number of dissociated ligands.

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Exploring organometallic molecules by electronic structure methods

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Organometallic molecules such as cobalt tricarbonyl nitrosyl, $\text{Co}(\text{CO})_3\text{NO}$, tungsten hexacarbonyl, $\text{W}(\text{CO})_6$, and dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, are investigated using various electronic structure methods. The results obtained from different density functionals are compared to results derived from post Hartree-Fock methods in order to determine a reasonable ratio of accuracy to computational cost. Also the basis set dependence will be in the focus of this study. Properties to be calculated are the geometrical parameters, bond dissociation energies, electrostatic features, ionization energies and electron affinities.

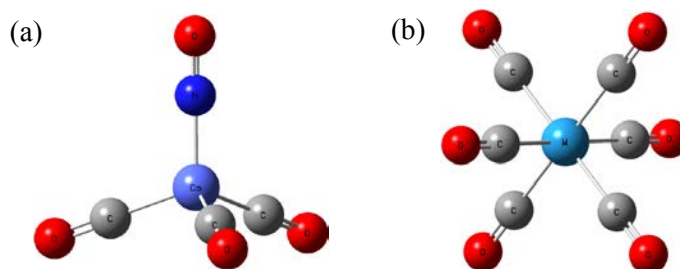


Figure 1: Schematic structures of (a) tungsten hexacarbonyl and (b) tungsten hexacarbonyl.

Acknowledgements

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Transport of electrons through a long metallic microcapillary: characterization of the outgoing low-energy electron beam

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The guiding of charged particles – highly charged ions – by insulating nanocapillaries has been firstly reported in 2002 [1] and has been attracting a large attention since then, partly due to potential applications in ion transport [2]. The pioneering work on electron guiding through insulating capillaries has been reported recently [3,4] and the electron guiding phenomena has been discussed in detailed nowadays [5,6]. The aim of the present research is to investigate the electron transport by metallic high-aspect ratio capillaries and their potential use for a robust, spatially well-determined, low-energy electron source, which can be efficiently applied to study electron driven molecular processes under different environmental conditions.

In this work we have investigated transmission of 150 eV incident electrons through a single stainless steel microcapillary (0.9 mm diameter and 19.5 mm length – the aspect ratio of about 22). The intensity of the outgoing electron current has been measured as a function of both the incident beam angle with respect to the capillary axis (tilt angle) and the kinetic energy of outgoing electrons. The “quasi-monochromatic” incident electron beam produces a wide distribution of outgoing electrons, spanning down to practically 0 eV. At large tilt angles (when the direct beam is suppressed due to the close collision with the inner wall of the capillary) this distribution is determined by elastic electron scattering, inelastic processes and secondary electron production. It is, however, interesting that the dependence on the tilt angle changes with the outgoing kinetic energy, and low-energy electrons may dominate at larger tilt angles.

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- [1] N. Stolterfoht et al., *Phys. Rev. Lett.* **88** (2002) 133201.
- [2] T. Ikeda et al., *J. Phys. Conf. Series* **399** (2012) 012007.
- [3] A. Milosavljević et al., *Phys. Rev. A* **75** (2007) 030901.
- [4] S. Das et al., *Phys. Rev. A* **76** (2007) 042716.
- [5] A. R. Milosavljević et al., *Nucl. Instrum. Meth. B* **279** (2012) 190.
- [6] K. Schiessl et al., *Phys. Rev. Lett.* **102** (2009) 163201.

Single-source precursors for the synthesis of nanostructured crystalline materials

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Nanotechnology has established a remarkable development, but one of the greatest challenges to achieve is still the complete control over the materials intrinsic properties. At present, the synthesis, combination and manipulation in a nanoscale level can allow this control and several methodologies can be proposed to achieve this goal.

In this work, the use of two distinct single-source precursors [1,2], for the synthesis of several nanocrystalline particles, including semiconductor crystallites, films, composites and hybrid structures is described. The preparation and characterization of nanocrystalline semiconductors, type M_xS_y , using single-molecule precursors, metal-dithiocarbamates (including Ag, Au, Bi, Cd, Co, Cu, Ni, Pt and Pd) and related molecular compounds containing both elements of the semiconductor, is presented and discussed. The hydrothermal preparation of particles and tubular structures of metal oxides, *e.g.* TiO_2 and SnO_2 , doped and co-doped with transition metals, using distinct single-source precursors, will be also presented. Additionally, nanocomposite materials can be easily obtained by a combination of several methodologies.

Acknowledgments

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References

- [1] O.C. Monteiro, H.I. S. Nogueira, T. Trindade, *Chem. Mater.* **13**, (2001) 2103
- [2] E. K. Ylhainen, M.R. Nunes, A.J. Silvestre, O.C. Monteiro, *J Mater Sci* **47**, (2012) 4305

Electron ionization and dissociative electron attachment to trimethyl borate

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We report a combined experimental and theoretical study of electron impact ionization (EII) to trimethyl borate $B(OCH_3)_3$ molecule. The electron impact ionization experiment [1] was carried out using crossed beams technique under single collision conditions with mass spectrometric analysis of the ions. The incident electron beam was generated by a trochoidal electron monochromator, the molecular beam was produced by effusion of the gas through a stainless steel capillary, the charged products were extracted by a weak electric field into a quadrupole mass spectrometer. The experimentally determined ionization energy of $B(OCH_3)_3$ is 10.33 ± 0.15 eV [2]. The appearance energies of dominant fragment ions formed via OCH_3 and CH_3 group cleavages were also determined. The experiment was supported by complex energy calculation using G3 quantum chemical method [3] to determine the ionization energy and the reaction enthalpies leading to the experimentally observed products. The calculated reaction enthalpies were compared with experimental AE's and the ionic structures were assigned to particular ion peaks on the basis of these calculations. On the basis of experimental and theoretical values we have determined bond dissociation energies for cations. Additionally, dissociative electron attachment to $B(OCH_3)_3$ has been investigated. We were able to detect only one negative ion $(OCH_3)^-$ at very low intensity formed via broad resonance at 7 eV, however published for first time via DEA to $B(OCH_3)_3$.

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[1] M. Stano, Š. Matejčík, J.D. Skalný and T.D. Märk, *J. Phys. B - At. Mol. Opt. Phys.* **36**, (2003), 261

[2] P. Papp, M. Lacko, D. Mészáros, M. Stano, P. Mach and Š. Matejčík, *Int. J. Mass. Spec.*, article accepted, recently proofs are expected.

[3] L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov and J.A. Pople, *J. Chem Phys.* **109**, (1998), 7764

Towards pure and compact FEBID deposits via e-beam assisted H₂O purification at room temperature

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During recent years, focused electron beam induced deposition (FEBID) has made significant progress with respect to potential applications ranging from passive devices, such as plasmonic gratings, towards active concepts like mechanical, magnetic or chemical sensing. Beside the undoubted advantages of FEBID as direct write tool with spatial nanometer resolution the limitations due to low material purity still remain. Successful attempts of purifying metal containing deposits have been demonstrated, mostly using a purification gas together with elevated temperatures [1] although another issue remained: an often porous deposit morphology which complicates the fabrication of very small but still compact structures as often needed for nano-applications. Recently, it has been demonstrated that the key for high fidelity morphologies lies in the application of low temperatures during purification. It has been shown that electron beam assisted purification of Pt-C deposits with 50 °C oxygen gas leads to highly compact and nominally pure deposits with purification rates of about 6 min per μm^2 deposit footprint [2]. In this study we push this concept even further and demonstrate that water vapor can be used as purification gas at room temperature together with the e-beam. The results show that very high rates better than 1 min per μm^2 deposit footprint can be achieved together with nominally pure Pt structures. Furthermore, the deposits are found to shrink by about 60 vol. % but still maintain their original footprint shape. The surface roughness of such high fidelity is found to less than 1 nm (RMS) and no holes or cracks appear on the surface. The study is complemented by a systematic variation of e-beam parameters during purification (beam current, dwell time, and pixel point pitch) revealing that a localized pressure of 10 Pa is sufficient to provide close to reaction rate limited conditions with respect to the water adsorbates. Finally, transmission electron microscopy and electron energy loss spectroscopy has been used to identify the purification as bottom up process. By that a new and comparable simple purification strategy is introduced which does not require gas and / or substrate heating while water, as purification gas, is almost straight-forward in terms of technical implementation.

[1] S. Mehendale, J. J. L. Mulders, and P. H. F. Trompenaars, *Nanotechnology* **24** (14), (2013), 145303

[2] H. Plank, J.H. Noh, J. D. Fowlkes, B. Lewis, and P. D. Rack, *ACS Applied Materials and Interfaces*, doi 10.1021-am4045458, (2014)

Bond cleavage in amines by dissociative electron attachment

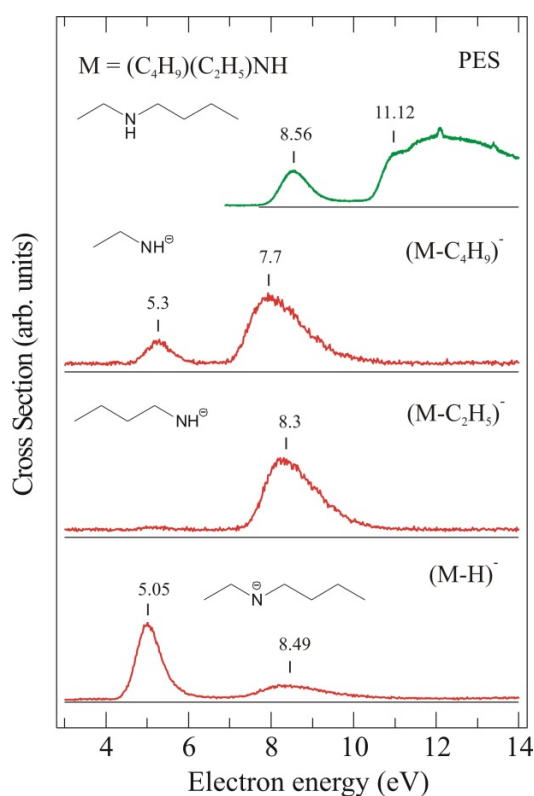
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The study of dissociative electron attachment (DEA) in oxygen containing compounds revealed a few interesting features [1, 2] and we studied the DEA of amines in order to see whether the trends encountered in alcohols are applicable to amines.

In the secondary amines, like ethylbutylamine (EBA), both N-C and N-H bonds are broken by DEA (Figure 1). The cleavage of N-H bond leads to the formation of $(M-1)^-$ ion in the DEA spectra, whereas the cleavage of N-C bond leads to the formation of $(M-R)^-$ ion, $R = C_2H_5$ or C_4H_9 .



There is a difference between the loss of ethyl radical and of butyl radical: while both processes are mediated by σ -Feshbach resonances, they occur at different energies, 7.7 eV for butyl and 8.3 eV for ethyl. It is an indication that the resonance is localized on the particular alkyl fragment. This suggestion is proved by the DEA spectra of diethylamine, triethylamine, diethylmethylamine, where the loss of ethyl radical occurs also at 8.3 eV, and the DEA spectra of dimethylbutylamine and tributylamine which show the loss of butyl at 7.7 eV. The assignment is supported by the energy relation with the grandparent cation.

Figure 1. DEA spectra and PE spectrum (topmost) of ethylbutylamine.

[1] B. C. Ibanescu, O. May, A. Monney and M. Allan, *Phys. Chem. Chem. Phys.* **9**, (2007). 3163

[2] B. C. Ibanescu and M. Allan, *Phys. Chem. Chem. Phys.* **10**, (2008). 5232.

Absolute cross sections of electronic excitation of furan

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Electronic excitation plays a key role in FEBIP as the first step of neutral dissociation, an alternative to the much studied DEA. Furan was chosen as a model compound for a ligand in FEBIP precursors and because our study will test existing calculations [1-3]. Relative differential cross sections at 0° were already measured in our group [4].

We measured absolute differential cross sections (DCSs) for elastic scattering and for electronic excitation of furan and extended existing measurements [1-3] to the near-threshold region. Two resonances are observed in the excitation of the lowest triplet state and we assign them as $^2(\pi_2, \pi^{*2})$ and $^2(\pi_1, \pi^{*2})$ valence core excited resonances. The cross sections for exciting the singlet states attain large values in the forward direction.

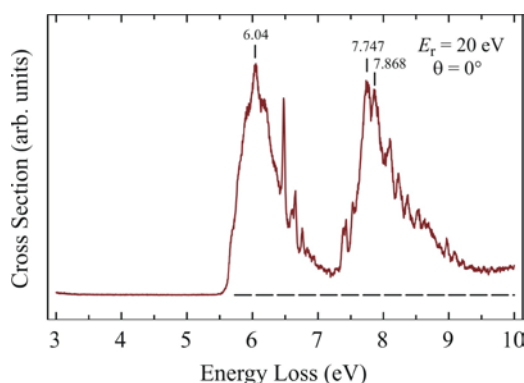


Figure 1. EEL spectrum of furan.

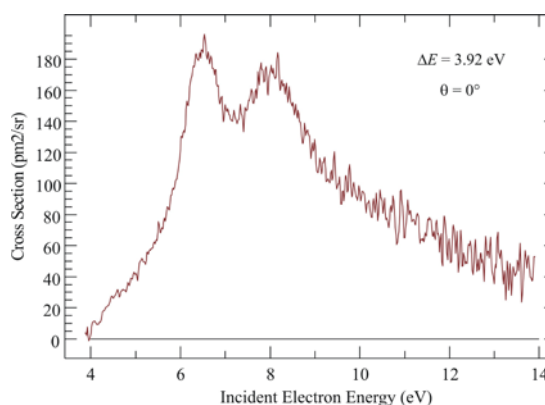


Figure 2. DCS for exciting the 1st triplet state.

- [1] R. da Costa, M. Bettega, M. Lima, M. Lopes, *Phys. Rev. A* **85**, (2012). 062706
- [2] J. B. Maljkovic, F. Blanco, R. Curik, G. Garcia, B. Marinkovic and A. Milosavljevic, *J. of Chem. Phys.* **137**, (2012). 064312
- [3] M. H. Palmer, I. C. Walker, C. C. Ballard, M. F. Guest, *Chem. Phys.* **192**, (1995). 111-125
- [4] K. Asmis, *PhD thesis, University of Fribourg, Switzerland* (1996)

Select purification and shape control approaches for EBID of Au, Co and SiO₂ for a range of applications.

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It is known by now that one of the major constraints of the EBID process is in poor chemical composition of as-deposited material, most often suffering from carbon contamination due to incomplete decomposition of the precursor molecule. This phenomenon obviously significantly affects functional properties of the deposited materials and limits their application range. To reduce the amount of contamination in the grown samples, specific purification steps should be applied, depending on the selected precursor.

In our recent research work, considering the actual demands for functional nanomaterials in the fields of micro- and nano-electronics, plasmonics, photonics, spintronics, bio-technology, bio-sensing and life sciences, we specifically focused on deposition, purification and shape control of Au, Co and SiO₂ materials from Me₂Au(acac), Co₂(CO)₈ and TEOS precursors respectively. For that reason we utilized following purification routes: post-deposition annealing (in air and reactive gas atmosphere), deposition onto heated substrates and deposition in the presence of reactive gases.

As a result, a substantial purity improvement was observed and a significant advancement was achieved in creation of high-purity gold [1, 2], cobalt [3, 4] and silicon dioxide nanoscale structures. Extensive analysis of physical properties showed close correlation with those of bulk and thin film materials. Some application examples will be shown.

[1] A.V. Riazanova, Y.G.M. Rikers, J.J.L. Mulders and L.M. Belova, *Langmuir* **28**, (2012). 6185-6191

[2] A.V. Riazanova, J.J.L. Mulders and L.M. Belova, *Mater. Res. Soc. Symp. L: Nanoparticle Manufacturing, Functionalization, Assembly, and Integration* **1546**, (2013). doi: 10.1557/opl.2013.620

[3] J.J.L. Mulders, L.M. Belova and A. Riazanova, *Nanotechnology* **22**, (2011). 055302

[4] L.M. Belova, E.D. Dahlberg, A. Riazanova, J.J.L. Mulders, C. Christophersen and J. Eckert, *Nanotechnology* **22**, (2011). 145305

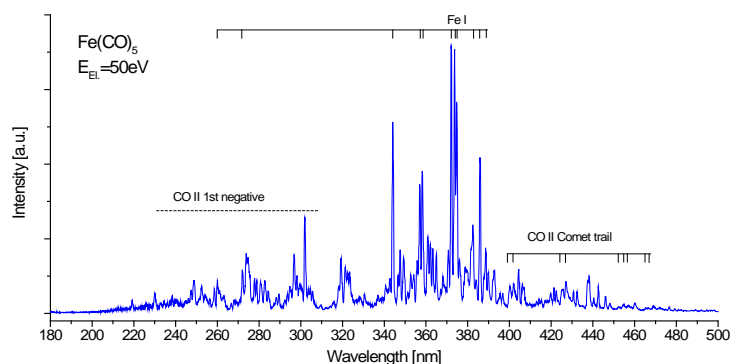
Dissociative Excitation of $\text{Fe}(\text{CO})_5$ Studied Using Electron Induced Fluorescence Apparatus

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The cross-beam experiment electron induced fluorescence apparatus (EIFA) in our laboratory, allows electron induced fluorescence (EIF) and dissociative excitation (DE) studies to molecules. These processes are initiated by electron impact. In recent years we have investigated several molecules [1-2]. The EIFA apparatus offers possibility to measure emission spectra of the molecules initiated by electron impact and the excitation-emission cross section measurements. In this work we present the results of dissociative excitation studies to organo-metallic molecule $\text{Fe}(\text{CO})_5$. In the Figure below we show the electron induced spectrum of $\text{Fe}(\text{CO})_5$ obtained with 50 eV electrons in the wavelength range between 180 nm and 500 nm with 0.8 nm optical resolution (200 μm slits of the optical monochromator). In this spectral range we have detected emission from Fe, C and O atoms and ions and CO and CO^+ bands. Further we will present excitation-emission cross sections for several DE channels originating from this molecule.



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- [1] J. Országh, M. Danko, A. Ribar, Š. Matejčík, *Nuc. Inst. Meth. Phys. Res. B* **279** (2012) 76–79
 [2] M. Danko, J. Országh, M. Ďurian, J. Kočíšek, M. Daxner, S. Zöttl, J. B. Maljković, J. Fedor, P. Scheier, S. Denifl, and Š. Matejčík, *J. Phys. B: At. Mol. Opt. Phys.* **46** (2013) 045203

FEBIP and FIBIP as tools for nanodevice prototype

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In the last two decades, the development, fabrication and characterisation of 1D nanostructures (nanotubes, nanowires, nanobelts, ...) have received large efforts because of their possibility of being used as potential building blocks of new devices and circuit architectures, thanks to the effects of their reduced physical size and the possibility of well controlling their chemical characteristics [1]. The growth can, nowadays, be relatively well controlled and the structural properties and chemical properties can be easily extracted with nowadays high resolution spectroscopic methods. However the number of papers dealing with the extraction of electrical parameters of such materials and, even more, with their manipulation, positioning and contacting for the fabrication of nanodevices and electronic systems, which include control and read-out electronics, based on them is still quite scarce. Additionally, there is still a large gap to bridge to incorporate such devices into real life applications.

In this work we report the activity carried out on the development, fabrication and test of advanced gas nanosensors prototypes based on individual metal-oxide nanowires. For this, vapor-liquid-solid (VLS) grown defect-free monocrystalline SnO₂ nanowires, with radii ranging from few ten to few hundred nm will be used [2]. The production of the nanodevices involved controlled dispersion and manipulation of the nanowires on top of photolithographically prepatterned microelectrodes, prepared either on bulk or on suspended substrates, and the contact fabrication using FEBIP and FIBIP, employing a metalorganic precursor inside the machine and allowing high spatial precision [3].

[1] M. Law, J. Goldberger, P. Yang, *Annu. Rev. Mater. Res.* 34 (2004) 151.

[2] S. Mathur, S. Barth, H. Shen, J. C. Pyun, U. Werner, *Small* 1 (2005) 713.

[3] F. Hernandez-Ramirez, A. Tarancon, O. Casals, J. Rodriguez, A. Romano-Rodriguez, J. R. Morante, S. Barth, S. Mathur, T. Y. Choi, D. Poulidakos, V. Callegari, P. M. Nellen, *Nanotechnol.* 17 (2006) 5577.

Etch masks for pattern transfer made by Electron Beam Induced Deposition

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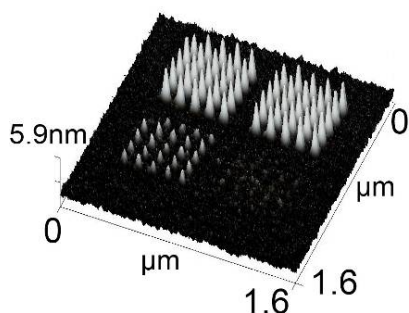
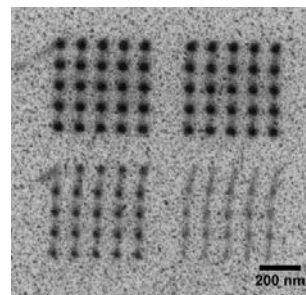
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Resist-based lithographic techniques do not routinely provide sub-10nm resolution. The project Single Nanometer Manufacturing for beyond CMOS devices (SNM) is aimed at achieving that, using Nanoimprint Lithography (NIL). The NIL stamps will be fabricated using both Scanning Probe Microscopy (SPM) and Electron Beam Induced Deposition (EBID).

We are developing a system, that allows to perform parallel EBID. It consists of a Scanning Electron Microscope (SEM) equipped with a multi-beam electron source [2,3] and it may enhance the throughput by a factor of 196 compared to a regular SEM [4].

NIL finally requires UV transparent stamps that can be made by transferring a lithographically defined pattern into the stamp material. To gain some insight in transferring nano-patterns into an underlying substrate we used EBID to fabricate patterns that serve as etch masks in a subsequent plasma etching process.

The figure shows an EBID etch-mask consisting of four arrays of



dots, patterned using the MeCpPtMe₃ precursor, at 30 kV. We used a Si substrate, which is partially covered by a 30 nm Mo layer with a search pattern for easily locating the masks. These dots have sizes varying from 42 nm to 19 nm at a pitch of 100 nm. The figure on the left shows an AFM image of the same mask: the height of the pillars varies from 5.5 nm to 1 nm. We will report the initial results of the different etching processes performed on the EBID masks.

[1] We acknowledge support from the European Union under Grant Agreement No. 318804 (SNM)

[2] A. Mohammadi-Gheidari, C.W. Hagen and P. Kruit, *J. Vac. Sci. Technol.* B28, (2010) C6G5

[3] A. Mohammadi-Gheidari and P. Kruit, *Nuclear Instruments and Methods in Physics Research A* 645, 60 (2011)

[4] P.C. Post, A. Mohammadi-Gheidari, C.W. Hagen and P. Kruit, *J. Vac. Sci. Technol.* B29, (2011) 06F310

Focused Electron Beam Induced Deposited multi-material nanostructures

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Focused Electron beam induced deposition (FEBID) is a direct writing technique where a focused beam of high energy electrons are used to decompose precursor molecules to a spot on a substrate [1]. Shape and topology of the deposited material can be controlled by this mask-free, resist-free technique. This technique already produced various application specific devices such as FEBID MOSCAP [2], nano-magneto logic devices [3], nano gas sensor [4].

Multi-material structures have novel applications in different research areas including spintronics, semiconductor transistors, sensors etc. This work presents Electron Beam Induced Deposited multi-material (mainly gold and iron) in i) different layer and ii) as a co-deposition. In co-deposition, the working pressures have been varied to deposit gold and iron at the same time. 3kV acceleration voltage with 1nA beam current have been used to deposit 1 x 1 μm of gold-iron structures.

Scanning Electron Microscope, Magnetic and Atomic Force Microscope and Energy Dispersive X-Ray Spectroscopy have been utilized to investigate structural, morphological, magnetic and compositional properties of the deposited materials. Focused Ion Beam (FIB) has been used to make a cross-section in the deposited material to see the different layers and their corresponding features. A practical strategy have been proposed to increase the metal content of the deposited material. To conclude, potential applications of Au-Fe structures will be discussed.

[1] I. Utke, P. Hoffmann, and J. Melngilis, *J. Vac. Sci. Technol. B* **26** (2008), 1197.

[2] M.M. Shawrav, H. D. Wanzenboeck, D. Belic, M. Gavagnin, O. Bethge, M. Schinnerl and E. Bertagnolli, *Phys. Status Solidi A*. doi: 10.1002/pssa.201330133

[3] M. Gavagnin, H.D. Wanzenboeck, D. Belic and E. Bertagnolli, *ACS Nano*, **7** (1), (2013), pp 777-784

[4] F. Kolb, K. Schmoltner, M. Huth, A. Hohenau, J. Krenn, A. Klug, E. List and H. Plank, *Nanotechnology* **24**, (2013). 305501

Electron impact ionization of iron pentacarbonyl

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Electron impact ionization of $\text{Fe}(\text{CO})_5$ is studied using a crossed electron beam / molecular beam apparatus. The electron beam with resolution 150 meV (FWHM) is generated by trochoidal electron monochromator. Ions are formed under single collision conditions, mass selected by a quadrupole mass analyzer and detected in ion counting mode. Detailed description of the experiment can be found in [1].

Electron impact ionization $\text{Fe}(\text{CO})_5$ is associated with rich fragmentation pattern and formation of both singly and doubly charged ions. Fragmentation proceeds mostly by loss of one or more CO ligands. Complete decomposition of the molecule is relatively efficient and Fe^+ has one of the highest ion yields. Present work is focused on determination of appearance energies of parent and fragment ion formation. The results will be compared with previous studies [2,3].

This work was supported by the Slovak Research and Development Agency under Contract No. APVV-0733-11 and VEGA 1/0514/12. The authors would like to thank to the COST Action CM1301 CELINA. KW acknowledges support by the Slovak National Fellowship fund.

[1] M. Stano, S. Matejčík, J.D. Skalný, T.D. Märk, *J. Phys. B: At. Mol. Opt.* **36** (2003) 261–271.

[2] R. E. Winters and R.W. Kiser, *Inorg. Chem.* **3** (1964) 699-702.

[3] B.R. Conrad and R. Sridhar, *Can. J. Chem.* **56** (1978) 2607-2608.

Application of pulsed IR laser to Focused-Electron-Beam-Induced-Deposition

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In this work we present the study of pulsed IR laser with an application to Focused-Electron-Beam-Induced-Deposition (FEBID). In direct local patterning from metalorganic gas precursors, the purity of the deposit is a crucial issue. Whereas some of the adsorbed molecules like AuCIPF₃, Fe(CO)₅ and Co₂(CO)₈ decompose to the pure metal upon electron exposure [1-3], the remaining majority gives in general low metal content, leaving organic residuals, e.g. (CH₃)₃Pt-CpCH₃, Cu(hfa)₂, W(CO)₆, to name a few. It has been already shown that the purity of those materials can be significantly improved by local pulsed IR laser heating, which facilitates the desorption of the reaction by-products and does not cause photolytic dissociation of adsorbates [4]. Here we have been investigating to experimentally quantify the effect of local laser pulses on the substrate surface temperature as a function of laser power and laser pulse duration. We present first results obtained from finite element simulations compared to a change of resistance of gold nanowires due to heating during the laser operation.

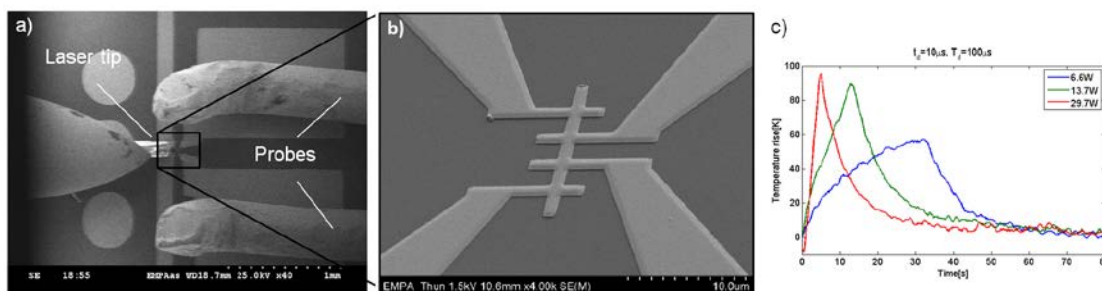


Figure 1: a) Setup for 4-point probe measurements - laser tip and Au electrodes connected to the external pins b) geometry of Au nanowire c) growth of surface temperature during the laser irradiation

- [1] I. Utke et al. J. Vac. Sci. Technol. B 18, 3168 (2000)
- [2] A. Fernández-Pacheco et al. J. Phys. D: Applied Physics 42, 055005 (2009)
- [3] H. Marbach et al. J Phys Chem C Nanomater Interfaces. 29; 117(34): 17674–17679 (2013)
- [4] N.A. Roberts, et al. Nanoscale 5, 1, pp 408-415 (2013)

Is Co_mO_n nanoparticle a precursor for the electron driven processes? Ab initio study

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Currently, metal nanoparticles, in particular those with magnetic properties, receive much attention due to their peculiar electronic, optical, catalytic, and magnetic properties [1-2]. In this content, the Co nanoparticles are studied very intensively. The application of these particles is ranging from ultrahigh density recording media to medicine and, in addition, they are traditional precursors of anode materials in Li-ion rechargeable batteries and an effective catalyst in the reduction of SO_2 by Co and NO by methane [3]. The particles could be used in high-density data storage devices and magneto-optical sensors. In order to achieve challenging technological goals, the magnetic particles need to be supported or embedded in other materials such as semiconductors or insulators. However, there are proved to be more difficult to prepare monodispersed nanoparticles by the traditional method because the synthesis process is more complex [4]. Our recent investigations reveal that the stability of these Co compounds increases with the increase of the number of O atoms in the particle. The results of these investigations proved also that magnetic properties of the Co nanoparticles are oxygen-atom-dependent, i.e. the Co nanoparticles could lose their magnetic properties due to oxidation [5]. It allows us to explain why the Co nanoparticles obtained is covered with thin layer of CoO. At present time, Focused Electron Beam Induced Deposition (FEBID) is very promising deposition technique for nanofabrication, although it relies on precursors that are not optimized for the electron driven process. Hence, we would like to perform ab initio simulation of the fragmentation processes of the Co_6O_n ($n=7-9$) and Co_{22}O_n , Co_{18}O_n nanoparticles to obtain knowledge do the Co shell-core nanoparticles could be applied to the electron induced fragmentation mechanisms occurred in FEBID to cover surface by the - pure Co nanoparticles. In this sense, the energy of the fragment appearance, the activation energy and product of fragmentation are investigated. Theoretical method is used to predict both all possible fragmentation channels and other processes that could occur under electron impact of these nanoparticles.

- [1] P.J. Reynolds (Ed.), On Cluster and Clustering, Elsevier Science Publisher, Amsterdam (1993)
- [2] P. Gambardella, S. Rusponi, M. Veronese, S.S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller,
- [3] D. A. Resnick, K. Gilmore, Y. U. Idzerda, et al., *Journal of Applied Physics*, **99**, (2006). 08Q501.1
- [4] G.H. Wen and et al., *Journal of Magnetism and Magnetic Materials*, **270**, (2004). 407
- [5] J. Tamuliene, R. Vaisnoras, G. Badenes, L.M. Balevicius, *Journal of Nanomaterials*, **2009** (2009), Article ID 308276, 7 pages <http://dx.doi.org/10.1155/2009/308276>

Characterization of π -allyl ruthenium tricarbonyl bromide as a potential EBID precursor by gas-phase and surface studies

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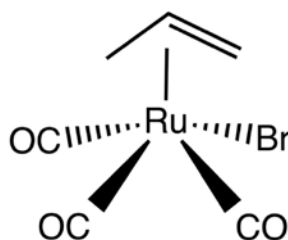
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Interactions of low energy electrons (LEEs) with precursor molecules are considered to have an important role in electron beam induced deposition (EBID).^[1] LEEs are abundant in EBID experiments, where a high energy primary electron beam impacts a surface that is continuously exposed to EBID precursor molecules. Due to the impact of the primary electron beam, secondary electrons are emitted from the surface, both inside and outside the radius of the incident electron beam.^[2] Two possible candidate channels for LEE-induced molecular dissociation in EBID are dissociative electron attachment (DEA) and dissociative ionization. The former is a resonant process that typically occurs at electron energies below 10 eV and can have very high cross sections close to 0 eV.^[3] The latter is a non-resonant process, generally with an onset slightly above the ionization limit of the respective precursor molecule.^[1] These processes are likely to contribute to adverse effects such as deposit broadening and co-deposition of ligands and ligand fragments from the organometallic precursor molecules. The ultimate goal of this research is to perform a systematic study on the role of LEEs in precursor molecule dissociation in both the gas phase and the condensed phase, and thus distinguish the dominating processes for different molecular classes. Additionally, while chemical vapor deposition (CVD) precursors have been extensively used as EBID precursors, this research looks to define novel organometallic compounds as potential EBID precursors.

This poster will present preliminary gas phase and surface science studies on an organometallic precursor molecule; π -allyl ruthenium tricarbonyl bromide (see figure), which was synthesized and characterized for its potential use as a ruthenium source in EBID. While the gas phase studies aim at determining the energetics and branching ratios of all involved DEA processes and compare these to the respective DI processes, the surface studies aim at characterization of the deposit and analyses of the desorbing fragments by using x-ray photoelectron spectroscopy (XPS) and mass spectrometry (MS). Here we compare the gas phase and surface studies and discuss these in relation to the role of the LEEs in the formation of a deposit when this molecule is exposed to high energy electrons under standard EBID processing conditions.



[1] S. Engmann, M. Stano, Š. Matečik, and O. Ingólfsson. *Phys. Chem. Chem. Phys.* **14**, (2012). 14611-14618.

[2] N. Silvis-Cividjian, C.W. Hagen, and P. Kruit. *J. Appl. Phys.* **98**, (2005). 084905.

[3] O. Ingólfsson, F. Weik, and E. Illenberger, *Int. Rev. Phys. Chem.* **15**, 133.

Fabrication of nanostructures with different precursors via Focused Electron Beam Induced Processing in UHV

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Focused electron beams are well suited to manipulate matter on the nanoscale. With our specific approach to focused electron beam induced processing (FEBIP), we are able to fabricate clean nanostructures on surfaces with full lithographic control from adsorbed precursor molecules. One fabrication technique in this regard is the electron beam induced deposition (EBID) [1], in which a precursor gas adsorbs on a substrate and is locally decomposed by a focused electron beam. Another concept is the electron beam induced surface activation (EBISA) [2], where the irradiated surface areas are active towards the catalytic decomposition of particular precursor molecules. The corresponding deposits might continue to grow autocatalytically upon prolonged dosage of the precursor. With metal-organic precursors such as iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), titanium(IV) tetraisopropoxide (TTIP) and cobalt tricarbonyl nitrosyl ($\text{Co}(\text{CO})_3\text{NO}$), we achieved the fabrication of clean metallic or metal oxide nanostructures with lateral dimensions as small as 10 nm [1-3].

In this contribution, we review the results of the FEBIP experiments with the three different precursors mentioned above. Their particular properties in respect to FEBIP techniques will be compared and discussed. For example $\text{Fe}(\text{CO})_5$ can be used in both EBID and EBISA on different surfaces, yielding very clean (>90%) iron nanostructures, while $\text{Co}(\text{CO})_3\text{NO}$ and TTIP are not compatible with FEBIA on the substrates tested so far.

[1] T. Lukaszcyk et al, *Small*, 4(2008), 841;

[2] M.-M. Walz et al., *Angw. Chem. Int. Ed.*, 49 (2010), 4669;

[3] M. Schirmer, et al., *Nanotechnology*, 22(2011). 085301;

On the electron-induced dissociation of cis-platin

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Focused electron beam induced processing is an additive direct-write lithography technique, used for instance for mask repair and circuit editing. However, to increase its applicability and develop it to its full potential, it is crucial to develop novel precursors that yield higher quality products. The requirements for better precursors are stringent. Obviously, they need to yield material of the desired quality. But at the same time, the vapor pressure needs to be sufficient to get the precursor into the gas phase, the compound needs to be stable enough for medium- or long-term storage, it should not be corrosive and it should not lead to unwanted etching of the sample.

To a limited extent we know which types of ligands meet these requirements. Arguably, carbonyl (-CO) ligands perform best so far, yielding deposits with a metal content of about 50% (depending on the writing conditions). Examples are $\text{Fe}(\text{CO})_5$ and $\text{Co}_2(\text{CO})_8$. Halides, the ligands used in e.g. WF_6 or AuCl_3 , are generally easily removed by electrons, but they etch and damage the sample. Methyl ligands (-CH₃) are effective in some cases (such as MeCp-Pt-Me_3), but ineffective in other cases (such as $\text{Sn}(\text{CH}_3)_4$). To find a precursor that meets all requirements, it is important to explore electron-induced chemistry to identify suitable ligand types.

We will present the results of experiments with cis-platin, $(\text{NH}_3)_2\text{-Pt-Cl}_2$ [1] While cis-platin may not be directly used as precursor (for instance due to a low vapor pressure), it is likely to reveal if the NH_3 -ligands can be removed by electrons.

Our experiments show that $(\text{NH}_3)_2\text{PtCl}_2$ is very sensitive to electrons. Cis-platin crystals are faceted and change into a spherical shape directly when exposed to the electron beam. Upon continued irradiation, the crystals decompose continuously until they reach a stable state. We have measured the effect of electron irradiation with energy-dispersive X-ray spectroscopy, electron energy loss spectroscopy and diffraction. This reveals that both nitrogen and chlorine are removed from the crystal. This strongly suggests that NH_3 is a suitable ligand type for novel precursors for focused electron beam induced processing.

[1] J. Kopyra, C. Koenig-Lehmann, I. Bald, E. Illenberger, *Angew. Chem. Int. Ed.* **48** (2009) 7904

Modelling the electron-induced dissociation of Ni(PF₃)₄ and Pt(PF₃)₄ with density functional theory

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Focused electron beam induced processing (FEBIP) is a versatile direct-write lithography process. Gaseous precursor molecules are introduced into the sample chamber of an electron microscope. The precursor adsorbs transiently on the sample surface, where it decomposes upon exposure to the electron beam. Depending on the precursor type, the dissociated molecules leave a residue and form a deposit or they react with the substrate to etch a hole or trench. FEBIP has gained increasing attention over the past decade as a fast and accessible lithography technique [1].

The major factor that limits the development of FEBIP is the precursor chemistry. There are only a few precursors available at the moment. Typically, FEBIP precursors either yield material of poor quality or they are thermally unstable, making them unsuitable for large-scale industrial use. The best performing precursor is, arguably, Pt(PF₃)₄, which yields deposits containing about 50% Pt [2]. If we want to develop FEBIP to its full potential, we need to design new compounds. To be successful, we will have to understand electron-induced chemistry at the fundamental level.

We use theoretical chemistry to reveal the dominant mechanisms in electron-induced chemistry. In particular, we present the results of density functional theory and coupled cluster calculations of Ni(PF₃)₄ and Pt(PF₃)₄ and their fragments. As Ni(PF₃)₄ is valence-iso-electronic with Pt(PF₃)₄ we expect that the chemistry will be similar, an assumption that is supported by experimental results. Generally the metal center does not dominate the dissociation mechanism [3] and the deposit compositions and morphologies obtained with the two precursors are roughly similar [4].

Our calculations show that both the Ni(PF₃)₃⁻ and the Pt(PF₃)₃⁻ anions are lower in energy than their parent compounds and that further dissociation is unfavourable. This implies that the formation of an anion and the loss of a single ligand is the only favourable reaction path. We will present the results on Ni(PF₃)₄ and Pt(PF₃)₄ and compare these to experimental data for Pt(PF₃)₄.

[1] I. Utke, P. Hoffman, J. Melngailis, *J. Vac. Sci. Technol. B* **26** (2008) 1197

[2] A. Botman, M. Hesselberth, J.J.L. Mulders, *J. Vac. Sci. Technol. B* **26** (2008) 2464

[3] J.D. Wnuk, S.G. Rosenberg, J.M. Gorham, W.F. van Dorp, C.W. Hagen, D.H. Fairbrother, *Surf. Sci.* **605** (2011) 257

[4] A. Perentes, G. Sinicco, G. Boero, B. Dwir, P. Hoffmann, *J. Vac. Sci. Technol. B* **25** (2007) 2228

Fabrication of Iron Nanostructures from Fe(CO)₅ by Electron Beam Induced Surface Activation of TiO₂(110)

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The controlled fabrication of structures on the nanoscale is a major challenge in science and engineering. Direct-write techniques like Electron Beam Induced Deposition (EBID) were shown to be suitable tools in this context. Recently, Electron Beam Induced Surface Activation (EBISA) has been introduced as a new focused electron beam induced processing (FEBIP) technique.¹ In EBISA, a surface is irradiated with the focused, high energy electron beam of a SEM or TEM under vacuum conditions (HV or UHV). The electron beam can trigger processes on the surface, which may result in surface activation. In a second step, a suitable precursor, e.g. iron pentacarbonyl Fe(CO)₅ or dicobaltoctacarbonyl Co₂(CO)₈,² is dosed onto the surface and selectively dissociates at the pre-irradiated, i.e. activated surface areas. In this way, a clean metallic deposit can be fabricated. In a second step, the initial deposit may continue to grow due to autocatalytic decomposition of further precursor molecules and form clean Fe nanostructures.

In this contribution, we report on FEBIA with the precursor Fe(CO)₅ on TiO₂(110). Microscopic (SEM and STM) and spectroscopic (AES) data reveal the corresponding activation mechanism on TiO₂(110).³ It is demonstrated by AES that the induced surface reactivity is linked to oxygen loss upon irradiation, via electron stimulated desorption (ESD). In addition, scanning tunneling microscopy of the activated areas on the TiO₂(110) surface reveals a high degree of irradiation-induced disorder for structures that are active towards the decomposition of Fe(CO)₅. Isolated defects, which are commonly found even on well-prepared TiO₂(110), also show (reduced) activity in line with the proposed activation mechanism.

¹ M.-M. Walz et al., *Angew. Chem. Int. Ed.* **49** (2010), 4669

² K. Muthukumar et al., *Beilstein J. Nanotechnol.* **3** (2012), 546

³ F. Vollnhals et al., *J. Phys. Chem. C* **117** (2013), 17674

Electron energy dependent fragmentation pathway of copper(II)acetylacetonate

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Organometallic compounds containing hexafluoroacetylacetonate ligands **1a** (Figure 1) are possible precursors for FEBID. Unfortunately, this compound usually yields deposits that are contaminated with carbon, oxygen and fluorine. Less attention has been paid to fully hydrated acetylacetonates **1b** due to their lower vapor pressure. However, exchange of fluorine by hydrogen may significantly alter the electron-induced fragmentation. We have therefore performed a detailed gas phase study on the electron induced fragmentation of **1b** including both negative and positive ion formation.

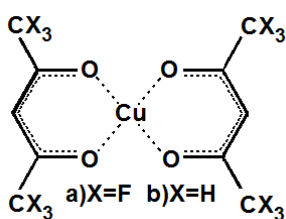


Figure 1

Mass spectra of **1b** recorded at different E_0 do not vary significantly between 40 eV and 250 eV with the main neutral fragments being radicals as in **1a**. However, some fragments disappear at lower E_0 and other fragments become dominant. Below 20eV, these dominant products can be attributed to rearrangement reactions leading to closed shell fragments that were not observed in the case of **1a**.

Finally, below the ionization threshold (<10eV), dissociative electron attachment (DEA) leads to loss of an acetylacetonate anion. In contrast to **1a** [1], no other fragmentation processes were observed at these low E_0 . The dissociation behavior of copper(II) acetylacetonate at low E_0 might thus be more favourable because no other non-volatile fragments are formed by DEA and DI fragmentation leads dominantly to less reactive volatile fragments. In conclusion, low energy secondary electrons that play an important role in FEBID induce significantly different reactions of the two compounds.

[1] S. Engmann, B. Ómmarson, M. Lacko, M. Stano, Š. Matejčík, O. Ingólfsson, J. Chem. Phys. 138, 234309 (2013).

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Reactive gas flooding for FIB - SIMS

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Nano-analytical techniques and instruments providing both excellent spatial resolution and high-sensitivity chemical information are of extreme importance in materials science and life sciences for investigations at the nanoscale. In order to get chemical information with a highest sensitivity and highest lateral resolution, we have investigated the feasibility of performing SIMS on FIB instrumentation, on the Helium Ion Microscope and on Transmission Electron Microscopes and we have developed dedicated prototype instruments.

In order to reach good detection limits when probing very small voxels in imaging applications, the ionisation probability of the sputtered atoms and molecules needs to be maximised. When using primary ion species such as Ga or noble gases, the intrinsic yields are low compared to the ones found in conventional SIMS. However, the yields may be drastically increased by using reactive gas flooding during analysis, namely O₂ flooding for positive secondary ions and Cs flooding for negative secondary ions [1-3]. Our results show that both negative and positive ion yields obtained with Ga⁺ bombardment are increased by up to 4 orders of magnitude when using such reactive gas flooding. This optimisation of secondary ion yields leads to detection limits varying from 10⁻³ to 10⁻⁶ for a lateral resolution between 10 nm and 100 nm (Figure 1).

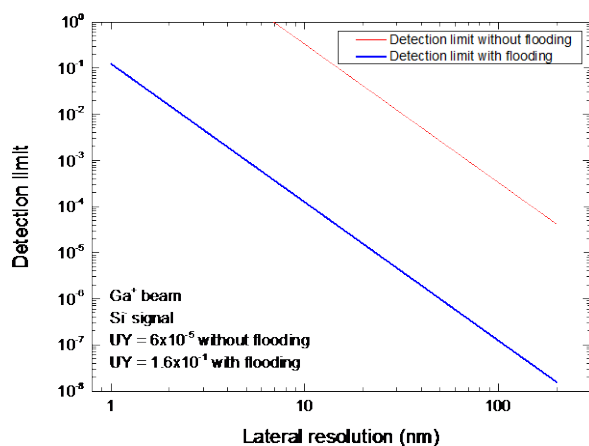


Figure 1: Detection limit using a Ga⁺ FIB with and without Cs⁰ flooding vs. minimum feature size: example for the detection of Si.

The results are very encouraging and the prospects of performing SIMS in combination with these high-resolution imaging and nanopatterning instruments are very interesting. In addition, the combination of high-resolution microscopy and high-sensitivity chemical mapping on a single instrument represents a new level of correlative microscopy.

- [1] P. Philipp, T. Wirtz, H.-N. Migeon and H. Scherrer, *Int. J. Mass. Spectrom.* **253** (2006) 71
- [2] T. Wirtz, N. Vanhove, L. Pillatsch, D. Dowsett, S. Sijbrandij and J. Notte, *Appl. Phys. Lett.* **101** (2012) 041601
- [3] L. Pillatsch, N. Vanhove, D. Dowsett, S. Sijbrandij, J. Notte, T. Wirtz, *Appl. Surf. Sci.* **282** (2023) 908

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