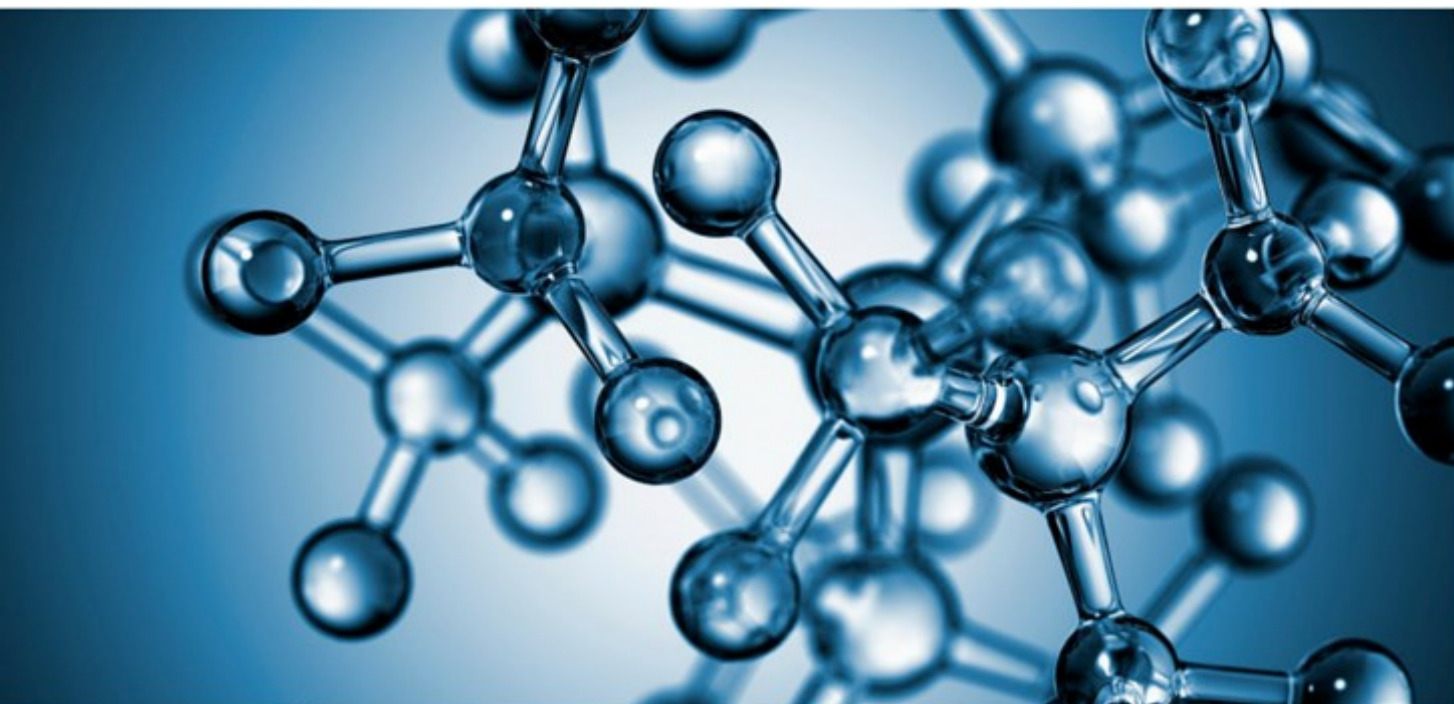




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# The 3rd CELINA Meeting

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Kraków, May 18-20, 2016



## The third Annual Meeting of COST Action CM1301 – Krakow, May 18-20, 2016

is organized by Siedlce University of Natural Sciences and Humanities jointly with the Academic Centre for Materials and Nanotechnology of the AGH University of Science and Technology in Krakow:



### Organizers:

#### International Organizing Committee:

Petra Swiderek (University of Bremen, DE)  
Cornelis W. Hagen (Delft University of Technology, NL)  
Nigel Mason (The Open University, UK)  
Janina Kopyra (Siedlce University, PL)  
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#### Local Organizing Committee:

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Aleksandra Szkudlarek (ACMIN)  
Katarzyna Berent (ACMIN)  
Katarzyna Hnida (ACMIN)  
Kamila Kollbek (ACMIN)

## Accommodation and conference venue:

### **Accommodation:**

Novotel Krakow City West

Armii Krajowej Street 11

30-150 Kraków

Tel.: +48 12 622 64 00



### **Conference place:**

Academic Centre for Materials and

Nanotechnology AGH,

Kawiory Street 30, 30-059 Kraków

AGH University Campus, building D-16

Tel. +48 12 617 49 44



### **Lunches:**

Krakus

Reymonta Street 15

30-059 Kraków

1<sup>st</sup> floor (~500 meters from the  
conference place)



### **Conference dinner:**

Restaurant Morskie Oko

Plac Szczepański 8

30-011 Kraków

Tel. +48 12 431 24 23



Dear Colleagues,

welcome to Krakow and CELINA 2016, the Third Annual Meeting of the COST Action CM1301 on „Chemistry for Electron –Induced NANofabrication” organized by Siedlce University jointly with The Academic Centre for Materials and Nanotechnology AGH.

The previous annual meetings of the Action which were held in Erlangen (March 2014) and Bratislava (May 2015) were a great success and gathered together the leading scientists in the field from Europe and overseas countries.

CELINA 2016 meeting promises to be an exciting and stimulating conference with more than 60 participants. We will have the opportunity to follow 31 oral presentations and more than 25 posters presented by excellent experts in their fields. We are convinced that the meeting will offer the opportunity to discuss results at the forefront of electron-driven chemistry as relevant to FEBID which aims at the rational design and novel approaches to the synthesis of the improved precursor molecules. A particular focus of this meeting, represented by experts in Atomic Layer Deposition (ALD) highlights exciting novel approaches to control surface reactions. These bear the promise to also improve control over FEBID thus leading to ultimate resolution and composition of the deposits. We hope that the meeting offer a stimulating forum to discuss these subjects and also to establish new scientific collaborations and strengthen those that already exist.

We wish you all an inspiring meeting in Krakow.

Petra Swiderek

Chair of COST Action CM1301

Janina Kopyra

CELINA 2016 Chair

Dear Participants of the 3rd Cost Action CELINA Meeting,

On behalf of the Local Organizing Committee I would like to warmly welcome you to the Academic Centre for Materials and Nanotechnology of the AGH University of Science and Technology in Krakow.

I wish you a successful conference and many inspiring, fruitful discussions, which will be a starting point for further collaborations and networking. I hope that you will enjoy the time spent at our Centre and in our historical city of Kraków.

Professor Marek Przybylski

Director of the Academic Centre for Materials and Nanotechnology

## Conference programme:

Tuesday, 17th of May	
17:00	Registration starting (Novotel Hotel)
19:00	Welcome reception (Novotel Hotel)

Wednesday, 18th of May	
8:45 - 9:00	<i>Janina Kopyra, Petra Swiderek</i> Opening
Chairman: Ivo Utke	
9:00 - 9:40	<i>Hubertus Marbach (University Erlangen-Nürnberg, Germany)</i> Electron beam induced surface activation and chemical selectivity: new routes for the fabrication of well-defined nanostructures
9:40 - 10:00	<i>Katja Höflich (Max Planck Institute for the Science of Light, Germany)</i> Electron beam induced deposition of silver based nanostructures
10:00 - 10:20	<i>Alex Laikthman (Holon Institute of Technology, Israel)</i> Functionalization of WS <sub>2</sub> Nanoparticles by Ga Implantation using Focused Ion Beam
10:20 - 10:40	<b>Coffee break</b>
Chairman: Nigel Mason	
10:40 - 11:10	<i>Oddur Ingolfsson (University of Iceland, Iceland)</i> Unusual features in dissociative electron attachment to the heteronuclear FEBID precursor HFeCo <sub>3</sub> (CO) <sub>12</sub>
11:10 - 11:40	<i>Michael Huth (Goethe University Frankfurt, Germany)</i> Heteronuclear precursors for FEBID of alloys and intermetallic compounds
11:40 - 12:00	<i>Lionel Amiaud (Université Paris-Sud, France)</i> Low energy electron (LEE) induced dissociation of deposited potential copper precursors for Focused Electron Beam Induced Deposition (FEBID)
12:00 - 12:20	<i>Iwona Szymańska (Nicolaus Copernicus University in Torun, Poland)</i> Collision experiments of the low energy electrons with copper(II) carboxylate compounds
12:20 - 12:40	<i>Michal Lacko (Comenius University, Slovak Republic)</i> Electron attachment to copper(II) carboxylate compounds
12:40 - 14:40	<b>Lunch</b>
Chairman: Paulo Limao-Vieira	
14:40 - 15:00	<i>Piet Trompenaars (FEI Company, The Netherlands)</i> Oxygen Gas Injection for in-situ purification of Electron Beam Induced Depositions
15:00 - 15:20	<i>Filipe Ferreira da Silva (Universidade Nova de Lisboa, Portugal)</i> Electron interactions with chromium and tungsten FEBID precursors



15:20 - 15:40	<i>Jelena Maljkovic (University of Belgrade, Serbia)</i> Dissociative electron attachment to benzene chromium tricarbonyl
15:40 - 16:00	<i>Anita Ribar (Leopold-Franzens-Universität Innsbruck, Austria)</i> Low-Energy Electron Interaction with Tungsten Hexacarbonyl Clusters
16:00 - 16:20	<b>Coffee break</b>
16:20 - 19:00	<b>Poster Session</b>
17:00 - 19:00	<b>MC meeting</b>
19:00 -	<b>Individual dinner in the city</b>

<b>Thursday, 19th of May</b>	
<b>Chairman: Oddur Ingolfsson</b>	
9:00 - 9:40	<i>Simon Elliott (University College Cork, Ireland)</i> Introduction to Atomic Layer Deposition and the COST Action HERALD
9:40 - 10:10	<i>Armin Götzhäuser (Universität Bielefeld, Germany)</i> Nanopore Fabrication and Characterization by Helium Ion Microscopy
10:10 - 10:40	<i>Charlene Lobo (University of Technology Sydney, Australia)</i> Electron beam processes for surface functionalization and directed nanostructure assembly semiconductors
10:40 - 11:00	<b>Coffee break</b>
<b>Chairman: Petra Swiderek</b>	
11:00 - 11:30	<i>Hartmut Hotop (University of Kaiserslautern, Germany)</i> Michael Allan - electron impact spectroscopy at its best
11:30 - 12:00	<i>Ilya Fabrikant (University of Nebraska, USA)</i> Resonances and Threshold Effects in Electron Collisions with Molecules and Clusters
12:00 - 12:30	<i>Roman Curik (Academy of Sciences of the Czech Republic, Czech Republic)</i> Negative ion resonances of polyatomic molecules: are they relevant for search of FEBID precursors?
12:30 - 13:00	<i>Juraj Fedor (Academy of Sciences of the Czech Republic, Czech Republic)</i> Cluster-beam experiments and the insight they bring into FEBID
13:00 - 15:00	<b>Lunch</b>
15:00 - 18:30	<b>Conference excursion: Krakow Old Town Walk</b>
18:30 -	<b>Conference dinner</b>

Friday, 20th of May	
<b>Chairman: Cornelis Hagen</b>	
9:00 - 9:30	<b>Gian Carlo Gazzadi</b> ( <i>Nanoscience Institute – CNR, Italy</i> ) FEBID nanolithography for the realization of fundamental thought experiments
9:30 - 10:00	<b>Lyobov Belova</b> ( <i>Royal Institute of Technology, Sweden</i> ) Gas-assisted electron-beam-induced nanopatterning of high-quality titaniumoxide
10:00 - 10:20	<b>Jozef Lengyel</b> ( <i>Leopold-Franzens-Universität Innsbruck, Austria</i> ) Argon mediated ionization of Fe(CO) <sub>5</sub> molecules deposited on argon nanoparticles
10:20 - 10:40	<b>Matija Zlataar</b> ( <i>University of Belgrade, Serbia</i> ) Excited States of Pt(PF <sub>3</sub> ) <sub>4</sub> and Their Role in Focused Electron-Beam Nanofabrication
10:40 - 11:00	<b>Coffee break</b>
<b>Chairman: Hubertus Marbach</b>	
11:00 - 11:40	<b>Erwin Kessels</b> ( <i>Eindhoven University of Technology, The Netherlands</i> ) Introduction to atomic layer deposition (ALD) and its links with FEBIP
11:40 - 12:00	<b>Sangeetha Hari</b> ( <i>Delft University of Technology, The Netherlands</i> ) Combined top-down and bottom-up 3D nanofabrication
12:00 - 12:20	<b>Imre Szenti</b> ( <i>University of Szeged, Hungary</i> ) Fabrication of carbon nanostructures on metal deposits prepared by EBID
12:20 - 14:20	<b>Lunch</b>
<b>Chairman: Edward Szlyk</b>	
14:20 - 14:40	<b>Aleksandra Szkudlarek</b> ( <i>AGH University of Science and Technology</i> ) Granular metals prepared by FEBID from copper and gold metalorganic precursors for gas-sensing applications
14:40 - 15:00	<b>Andrey Solov'ov</b> ( <i>MBN Research Center at FiZ, Germany</i> ) Molecular Dynamics for Irradiation Driven Chemistry: Application to the FEBID process
15:00 - 16:00	<b>WG meetings</b>
16:00 - 16:20	<b>Coffee break</b>
<b>Chairman: Stefan Matejcik</b>	
16:20 - 16:50	<b>Mostafa Moonir Shawrav</b> ( <i>Vienna University of Technology, Austria</i> ) Focused electron beam induced surface reactions - from surface termination to etching
16:50 - 17:10	<b>Stefan Cwik</b> ( <i>Ruhr Universität Bochum, Germany</i> ) Application of tailored metal-organic precursors in Focused Electron Beam Induced Deposition (FEBID) of Iron Oxides (FeOX): Fe(tbaoac) <sub>3</sub> and Fe(pk <sub>i</sub> ) <sub>2</sub>

17:10 - 17:30	<i>Milos Rankovic (University of Belgrade, Serbia)</i> Design and performance of an instrument for gas phase electron spectroscopy of trapped molecular ions
17:30	<b>Closing remarks</b>
18:00 -	<b>Free evening</b>

<b>Saturday, 21st of May</b>	
9:00 -	Lab visits and discussions at ACMIN



# **Oral contributions**

## Electron beam induced surface activation and chemical selectivity: new routes for the fabrication of well-defined nanostructures

Hubertus Marbach <sup>1,\*</sup>

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In Focused Electron Beam Induced Processing (FEBIP) the generation of extremely small, pure nanostructures can be targeted with lithographic control [1, 2]. 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.<sup>1</sup> Recently we were able to expand the family of FEBIP techniques with the exploration of Electron Beam Induced Surface Activation (EBISA) [2-6]. 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 (AG). The feasibility of FEBIA with Fe(CO)<sub>5</sub> for different oxide surfaces, e.g. silica (Fig 2) [3] and TiO<sub>2</sub>(110) [4] will be reported and expanded to porphyrin layers on Ag(111) [5] and even surface-anchored metal-organic frameworks. In addition the EBISA process is also not limited to the precursor Fe(CO)<sub>5</sub> but works also for example for Co(CO)<sub>3</sub>NO [6]. With our specific “surface science” approach to FEBIP, i.e. to work in an ultra-high vacuum environment, we are able to fabricate basically pure metallic deposits [2-6]. One particular interesting effect is the chemical selectivity certain surfaces and surface modifications, e.g., Co(CO)<sub>3</sub>NO decomposes on pristine TiO<sub>2</sub>(110) whereas it remains unaffected by the corresponding (1x2) reconstruction, interestingly Fe(CO)<sub>5</sub> exactly behaves opposite, i.e. the precursor remains intact on the clean (1x1) surface but decomposes on the (1x2) reconstructed substrate. It will be discussed how such selectivity effects in combination with AG can be used for the controlled, parallel fabrication of clean metallic nanostructures.

[1] a) W.F. van Dorp, C.W. Hagen, *J. Appl. Phys.* **104** (2008) 081301 b) I. Utke, et al., *JVST B* **26** (2008) 1197; c) S. J. Randolph et al., *Crit. Rev. Solid State Mater. Sci.* **31** (2006) 55.

[2] H. Marbach, *Appl. Phys. A* **117** (2014) 987.

[3] a) M.-M. Walz et al., *Ang. Chem. Int. Ed.*, **49** (2010) 4669; b) *PCCP* **13**, (2011) 17333; c) *App. Phys. Lett.*, **100** (2012) 053118.

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

[5] F. Vollnhals et al., *Langmuir* **29** (2013) 12290.

[6] F. Vollnhals et al., *Beilstein J Nanotech.* **5** (2014) 1175.

## Electron beam induced deposition of silver based nanostructures

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The direct writing using a focused electron beam (FEBID) for the local decomposition of a precursor medium is a process which allows for the fabrication of truly three-dimensional structures on the nanometer scale. One important challenge, however, is the identification of appropriate precursors which allow for a deposition of the material of choice in combination with the full 3D capabilities e.g. for envisaged applications in nano-optics. In this respect the coinage metal silver is of particular interest since it shows a relatively high plasma frequency, and thus, excellent plasmonic properties in the visible range. However, silver FEBID is not trivial as the low vapor pressures of typical precursor candidates necessitates heating of the precursor reservoir to achieve reasonable gas supply as well as heating of the substrate to avoid condensation. Simultaneously thermal dissociation needs to be prevented. Out of three precursor substances tested two metal-organic compounds, namely Ag 3,3-dimethyl-1-butynyl (short: AgMe<sub>2</sub>Bu1) and Ag (2,2-dimethylbutanoato-κO)- (short: AgMe<sub>2</sub>Bu2) showed reliable results for deposition. AgMe<sub>2</sub>Bu1 exhibits low sensitivity to electron beam impact and extremely small vapor pressures resulting in very low deposition rates. In contrast, AgMe<sub>2</sub>Bu2 provided for reliable deposition of silver-based composites having atomic silver:carbon ratios of around 4:5 as determined by energy-dispersive X-ray diffraction. Interestingly, the silver deposition was accompanied by a strong autocatalytic activity resulting in the formation of pure silver crystals, especially in the halo region where the precursor ligands were not polymerized by electron beam impact. While such halo formation is unwanted in the growth of nanostructures it significantly enhances the silver content in planar deposits, which in turn can be optically described as ‘diluted’ silver by employing an effective medium model. Corresponding calculations in comparison to optical transmittance and reflectance spectra will be presented.

## Functionalization of WS<sub>2</sub> Nanoparticles by Ga Implantation using Focused Ion Beam

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Inorganic nanotubes and inorganic fullerene-like nanoparticles of WS<sub>2</sub> conserve their semiconductor and diamagnetic behavior of bulk WS<sub>2</sub> material. Implantation of metal atoms like Ga, Nb, Cl, Re, etc. into the crystal structure of these nanoparticles can change their electronic (semiconductor to metal transfer), magnetic (diamagnetic to paramagnetic transfer), and optical properties, surface characteristics, and chemical behavior. These parameters are of extreme interest during the last few decades as could be useful in many nanotechnology applications, like photovoltaics and optoelectronics, catalysts and sensors preparation, and even tribology and lubrication. For example, doping of WS<sub>2</sub> fullerene-like nanoparticles with Re atoms resulted in their improved lubrication properties due to increase in electrical conductivity which led to electrostatic mutual repulsion [1].

Focused ion beam (FIB) etching was already applied for ion implantation into different materials with the objective to apply this technology as an alternative method for fabricating semiconductor devices [2]. For WS<sub>2</sub> nanoparticles, the previously used Ga<sup>+</sup> doses of  $\sim 10^{17}$  cm<sup>-2</sup> induced damage and amorphization, as was evident from Scanning Electron Microscopy (SEM) images and from a decrease in the intensity of the characteristic Raman peaks. However, when decreasing the Ga<sup>+</sup> ion dose to  $1-3 \times 10^{15}$  cm<sup>-2</sup>, the resultant structural damage was minor and the characteristic bands in the micro-Raman spectra taken from ion-exposed WS<sub>2</sub> samples were mostly identical to the pristine WS<sub>2</sub> nanoparticles. Nevertheless, even at these low ion doses FIB irradiation, Ga<sup>+</sup> atoms penetrated to the nanoparticles to the concentrations of 0.3-0.6 at.%, (dependent on the dose and the nanoparticles type), as measured by EDS. Micro-Raman spectra of the FIB-treated materials showed appearance of a number of additional small peaks in the 180-300 cm<sup>-1</sup> region. These features can be attributed to the formation Ga-Ga and Ga-S bonds.

FIB-induced implantation of Ga to WS<sub>2</sub> nanoparticles to the concentrations listed above may considerably affect their electronic and electrical properties. In order to determine the modifications induced by the Ga<sup>+</sup> FIB irradiation in the WS<sub>2</sub> nanoparticles, various measurements will be applied like four point probe I-V electrical measurements, scanning tunneling spectroscopy (STS), SQUID magnetometry (superconducting quantum interference device), etc.

[1] L. Rapoport, A. Moshkovich, V. Perfilyev, A. Laikhtman, I. Lapsker, L. Yadgarov, R. Rosentsveig, R. Tenne, *Trib. Lett.* **45** (2012) 257.

[2] C. A. Volkert, A. M. Minor, *MRS Bulletin* **32** (2007) 389.

## Unusual features in dissociative electron attachment to the heteronuclear FEBID precursor $\text{HFeCo}_3(\text{CO})_{12}$

Oddur Ingólfsson<sup>1\*</sup>, Ragesh Kumar T P<sup>1</sup>, Sven Barth<sup>2</sup> and Ragnar Björnsson<sup>1</sup>

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The use of heteronuclear organometallic precursors in focused electron beam induced deposition (FEBID) is an attractive alternative to mixed gas or multiple gas inlet systems for the fabrication of alloy nano-structures.  $\text{HFeCo}_3(\text{CO})_{12}$  is such a heteronuclear precursor, that has been used in chemical vapour deposition of thin FeCo films [1], and was recently used in FEBID of FeCo nano-structures [2]. To our knowledge, this is the first time FEBID of alloy nano-structures has been conducted with a single (heteronuclear) precursor. In fact the authors report a typical 80% metal content of the deposits with 1:3 FeCo ratio.

Motivated by the success of these experiments and the notation of the role of low energy secondary electrons in FEBID (see e.g. ref [3] and references therein), we have set out to characterise low energy interaction with  $\text{HFeCo}_3(\text{CO})_{12}$  in the gas phase, more specifically it's decomposition through dissociative electron attachment and dissociative ionisation.

In the current contribution we discuss DEA to  $\text{HFeCo}_3(\text{CO})_{12}$ , which in fact shows some remarkable features.

The two main channels observed are the loss of the apical Fe-group as  $\text{Fe}(\text{CO})_4^-$  and to a lesser extent as  $\text{Fe}(\text{CO})_3^-$  and  $\text{Fe}(\text{CO})_2^-$  and sequential CO loss. In good agreement with the first channel, we find that the optimised structure of the molecular anion at the BP86/def2-TZVP level of theory is characterised by substantial elongation of the Fe-Co bonds and the conversion of one of the terminal Co-CO to a Fe-C(O)-Co bridging ligand. Furthermore, we find appreciable spin density at the apical Fe of the anion and the SOMO is found to have a strong antibonding Co-Fe character. Hence the calculations offer a consistent picture of our experimental observations of a prominent formation of  $\text{Fe}(\text{CO})_4^-$ .

The second channel, the sequential loss of the CO ligands extends from the loss of 1 and 2 CO close to 0 eV up to the loss of all 12 CO ligands close to 20 eV, i.e., about 12 eV above it's ionisation energy. To try to elucidate this remarkable observation we have calculated the state density of this compound and compared that to similar model compounds without the metal core (e.g. linear CO bridged  $\text{Co}_3(\text{CO})_{12}$ ) and with the naked metal core. For the carbonyl compounds we find high density of metal-CO anti bonding orbitals about 3 eV above the HOMO leading us to the preliminary interpretation that the attachment process proceeding the CO loss is partly associated with multiple electronic excitations followed by rapid energy dissipation through CO loss.

**Acknowledgments:** This work was supported by Icelandic Centre for Research (RANNIS) and the University of Iceland Research Fund and conducted within the framework of the COST Action CM1301 (CELINA)

[1] C. L. Czekaj-Korn, G. L. Geoffroy, Transformation of Organometallics into Common and Exotic Materials: Design and Activation. 157-164 (1988).

[2] F. Porrati, M. Pohlit, J. Müller, S. Barth, F. Biegger, C. Gspan, H. Plank, M. Huth, *Nanotechnology* **26** (2015) 475701.

[3] R. M. Thorman, R. Kumar T. P., D. H. Fairbrother, O. Ingólfsson, *Beilstein J. Natotechnol.* **6** (2015) 1904.

## Heteronuclear precursors for FEBID of alloys and intermetallic compounds

Michael Huth<sup>1\*</sup>, Lukas Keller<sup>1</sup>, Fabrizio Porrati<sup>1</sup>, Marc Hanefeld<sup>1</sup>, Paul Weirich<sup>1</sup> and Sven Barth<sup>2</sup>

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Heteronuclear precursors hold great potential for the direct-write nano-fabrication of alloys and intermetallic compounds. In recent work we could show that the precursor  $\text{HFeCo}_3(\text{CO})_{12}$  can be used for the fabrication of ferromagnetic nanostructures by focused electron beam induced deposition (FEBID) under a wide range of beam conditions and writing parameters [1]. In particular, metal contents in excess of 80 at% can be readily achieved under beam conditions suitable for high-resolution work.

In the first part of the presentation we will focus on follow-up work with the precursor  $\text{HFeCo}_3(\text{CO})_{12}$  in which we optimized the writing parameters with a view to obtain high-resolution nanostructures down to the 10 nm range. Particular emphasis will be put on the magneto-transport properties of two-dimensional nano-dot arrays of Fe-Co with different inter-dot spacings approaching the metal-insulator transition (MIT) from the insulating side. The presented results on the temperature-dependent conductance and the longitudinal magneto-resistance will be discussed in the framework of spin-dependent tunneling effects between ferromagnetic nanostructures.

The second part of the presentation will be devoted to a comparative study of the growth characteristics of the precursor  $\text{HFeCo}_3(\text{CO})_{12}$  and its structural equivalent based on Fe-Ru. In particular, the achievable metal content and overall composition of the deposits under optimized writing conditions obtained for the Fe-Ru precursor with the application of a semi-automatic optimization procedure [2-4] will be addressed. Special attention will be given to the degree of fidelity in transferring the writing pattern to the final deposit under various beam conditions. It is expected that recent work on relevant electron-induced dissociation channels of  $\text{HFeCo}_3(\text{CO})_{12}$  in the gas phase [5] will shed light on the growth characteristics observed by us under typical FEBID writing conditions.

[1] F. Porrati, M. Pohlitz, J. Müller, S. Barth, F. Biegger, C. Gspan, H. Plank, M. Huth, *Nanotechnology* **26** (2015) 475701.

[2] P. M. Weirich, M. Winhold, Ch. H. Schwalb, M. Huth, *Beilstein J. Nanotechn.* **4** (2013) 919.

[3] M. Winhold, P. M. Weirich, C. H. Schwalb, M. Huth, *Nanofabrication* **1** (2014) 86.

[4] M. Winhold, P. M. Weirich, C. H. Schwalb, M. Huth, *Microelectr. Engineering* **121** (2014) 42.

[5] Oddur Ingólfsson, private communication.

## Low energy electron (LEE) induced dissociation of deposited potential copper precursors for Focused Electron Beam Induced Deposition (FEBID).

L. Amiaud<sup>1</sup>; L. Sala<sup>1</sup>; C. Dablemont<sup>1</sup>; A. Lafosse<sup>1</sup>; M. Krzemińska<sup>2</sup> and I. B. Szymańska<sup>2</sup>

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FEBID needs precursor compounds combining properties that are challenging to gather in a single compound (stable and dissociable, volatile and physisorbable). Ideally, under electron bombardment, they should split into distinct types of fragment: light fragments that fully desorb and leave the surface on one hand, and a single pure metallic deposit on the other hand. Precursors used in Chemical Vapor Deposition (CVD) are proposed as possible precursors for FEBID, but their fragmentation under electron beam must be understood and this can generally not be deduced from thermal dissociation products. As these processes may be triggered by secondary LEE unavoidably produced under high energy beam, using LEE as primary particles can help disentangle the fragmentation-deposition process under electron bombardment.

We present first results of a study on LEE induced processing of potential precursors of a new class promising for CVD: [Cu<sub>2</sub>(EtNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CC<sub>3</sub>F<sub>7</sub>)<sub>4</sub>] and [Cu<sub>2</sub>(EtNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CC<sub>2</sub>F<sub>5</sub>)<sub>4</sub>].<sup>1,2</sup> The saturated solution of compounds were prepared in tetrahydrofuran and deposited on silicon wafer by Langmuir Blodgett technique. Infrared spectra recorded in Toruń (the complex film on the KBr plate) and High Resolution Electron Energy Loss Spectroscopy vibrational spectra, recorded in Orsay, are compared for the pristine compound before irradiation. Dissociation processes in the film are probed in Orsay, in e-solid experimental setup, by electron stimulated desorption analysis of neutral fragments.<sup>3</sup> Release of fluorocarbon compounds under LEE impact is observed above a threshold. Changes in HREELS spectrum after irradiation will be discussed.

[1] I.B. Szymańska, *Polyhedron* **50** (2013) 200.

[2] P. Piszczek, I.B. Szymańska, E. Talik, J. Heimann, *Chem. Vap. Depos.* **19** (2013) 251.

[3] J. Houplin, L. Amiaud, V. Humblot, I. Martin, E. Matar, R. Azria, C-M. Pradier, A. Lafosse, *Phys. Chem. Chem. Phys.* **15** (2013) 7220.



## Collision experiments of the low energy electrons with copper(II) carboxylate compounds

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The analysis of the electron-impact mass spectra of copper(II) perfluorinated carboxylates, CVD data for the  $[\text{Cu}_2(\text{}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{CR})_4]$  complexes [1,2], and the possibility of these compounds application in the electron induced deposition process caused that the collision experiments of low energy electron were carried out. The following pentafluoropropionate derivatives:  $[\text{Cu}_2(\text{}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (**1**),  $[\text{Cu}_2(\text{}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (**2**),  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (**3**), and  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (**4**) were chosen for the experiments.

The spectra in the positive mode were measured. For the fragments with the highest intensity the threshold energies were evaluated. In the case of  $[\text{Cu}_2(\text{}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (**1**) complex, the following ions were observed among others:  $[\text{C}_3\text{H}_4]^+$  40 m/e;  $[\text{C}_3\text{H}_5\text{N}]^+$  58 m/e;  $[\text{C}_4\text{H}_9\text{NH}]^+$  72 m/e;  $[\text{Cu}(\text{}^t\text{BuNH}_2)]^+$  136 m/e;  $[\text{NH}_3\text{O}_2\text{CC}_2\text{F}_5]^+$  180 m/e;  $[(\text{C}_2\text{F}_5\text{O})(\text{C}_4\text{H}_9\text{NH}_2)]^+$  208 m/e;  $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$  289 m/e;  $[\text{Cu}(\text{O}_2\text{CC}_2\text{F}_5)(\text{C}_4\text{H}_9\text{NH}_2) - \text{H}]^+$  298 m/e, and  $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)(\text{}^t\text{BuNH}_2)]^+$  362 m/e. The observed ions sequence and their intensities were different than registered in the standard EI MS experiments what suggests the heating rate influence on the fragments formation.

Moreover, the first time for the  $[\text{Cu}_2(\text{R}'\text{NH}_2)_2(\mu\text{-O}_2\text{CR})_4]$  complexes and  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (**4**) compound the energy dependent electron impact mass spectra in the negative mode (DEA) were measured. The highest number of the ions was observed at 0 eV e.g.  $[\text{C}_2\text{F}_4]^-$  100 m/e;  $[\text{O}_2\text{CC}_2\text{F}_4]^-$  144 m/e;  $[\text{O}_2\text{CC}_2\text{F}_5]^-$  163 m/e;  $[\text{Cu}(\text{O}_2\text{CC}_2\text{F}_5)_2]^-$  389 m/e;  $[\text{Cu}(\text{O}_2\text{CC}_2\text{F}_5)_3]^-$  552 m/e;  $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)_4]^-$  778 m/e.

Acknowledgments: This work was conducted within the framework of the COST Action CM1301 (CELINA) No. COST-STSM-CM1301-27805. Financing of this work was by the Slovak Grant Agency VEGA 1/0417/15 and by the Slovak Research and Development Agency, project Nr. APVV-0733-11.

[1] P. Piszczek, I.B. Szymańska, E. Talik, J. Heimann, *Chem. Vap. Dep.* **19** (2013) 251.

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

## Electron attachment to copper(II) carboxylate compounds

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Electron attachment and dissociative electron attachment (DEA) processes were investigated on pentafluoropropionate derivatives:  $[\text{Cu}_2(\text{}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ ,  $[\text{Cu}_2(\text{}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ ,  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ , and  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ . Experiment was performed by crossed electron and molecular beam apparatus equipped with quadrupole mass spectrometer [1], the solid and gel samples were sublimated into a vacuum chamber after heating up to 100 – 150 °C.

All the studied molecules have very similar DEA products (example in fig. 1), without a significant effect of different alkylamine ligands on the 4 molecules. A very common feature is that no DEA products with presence of alkylamine group were detected. A small effect of different alkylamine ligands of the 4 molecules were the relative abundances of resonances for  $\text{C}_2\text{F}_4^-$  and  $\text{O}_2\text{CC}_2\text{F}_5^-$ . All DEA products have a resonance mostly into region close to 0 eV, some strong other weak. Only for some products a second resonance is presented with threshold at ~2 eV with maxima at 4.5 eV followed by resonances at higher energies. For copper(II) pentafluoropropionate molecule some additional negative ions was detected.

Acknowledgments: This work was conducted within the framework of the COST Action CM1301 (CELINA). Financing of this work was by the Slovak Grant Agency VEGA 1/0417/15. This work was supported by the Slovak Research and Development Agency, project Nr. APVV-0733-11.

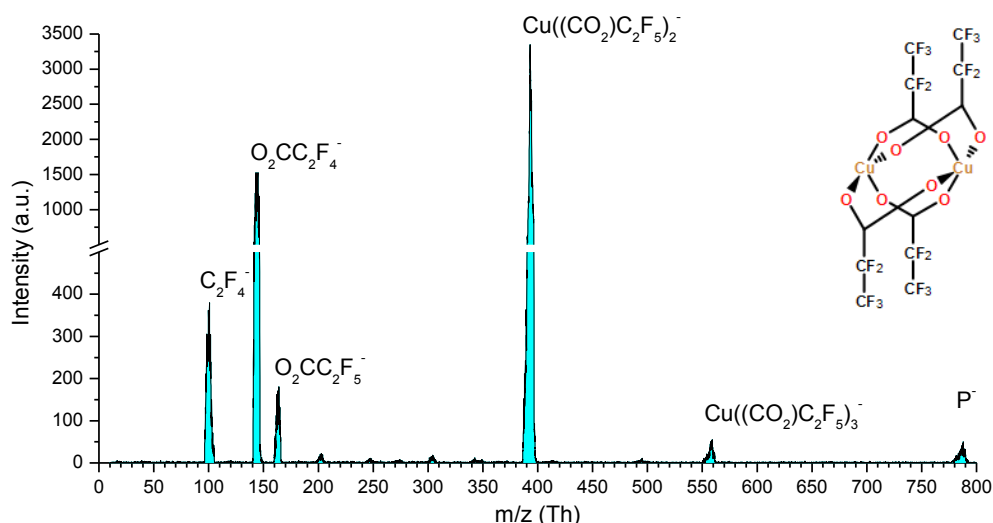


Fig. 1: Mass spectrum at electron energy near to 0 eV of copper(II) pentafluoropropionate.

[1] M. Stano, S. Matejcik, J.D. Skalny, T.D. Märk, *J. Phys. B: Atomic, Molecular and Optical Physics*, **36** (2003) 261.

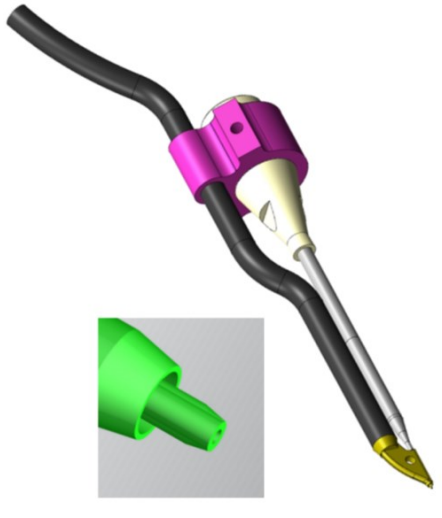
## Oxygen Gas Injection for in-situ purification of Electron Beam Induced Depositions

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In close cooperation with numerous academic partners in the past few years, significant improvements regarding purity of EBID structures have been achieved. Not only high purity platinum [1], gold [2] and palladium [3] depositions, but also high quality NiO [4], SiO<sub>2</sub> [5] and TiO<sub>2</sub> [6] EBID patterns can be produced in situ at room temperature by applying high flux oxygen under electron beam illumination. The oxygen will react with carbonaceous dissociation products of the precursor, creating volatile species, leaving a deposit with very low carbon content.



Either separate oxygen post-treatment, or a simultaneous precursor and oxygen supply during patterning can be used. Separate supply line and nozzle for the oxygen and the precursor gas can be used, or precursor and oxygen share a needle and nozzle and both gasses can be mixed inside the needle. In case of Pt and Au deposition a specific dual exit concentric add-on nozzle was used (picture).

In this presentation we summarize the results and we describe different modes of operation and engineering aspects, stating pros and cons.

- [1] E. Villamor et al., *Nanotechnology* **26**(2015) 095303.
- [2] S. Mehendale, et al., *Microelectro. Eng.* **141** (2015).
- [3] C. Mansilla Sanchez et al., to be published.
- [4] R. Córdoba et al., *Nanotechnology* **27** (2016).
- [5] A. Riazanova et al., *Nanotechnology* **25** (2014)155301.
- [6] A. Riazanova et al, *Nanotechnology* **27** (2016) 115304.

## Electron interactions with chromium and tungsten FEBID precursors

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Focused electron beam induced deposition (FEBID) is a technique capable of writing three-dimensional nanostructures on surfaces using electron driven reactions of organometallic compounds. The limitations in FEBID processes can be described as resolution due to the deposition out of the area of the primary beam electron and purity in metal of the deposit, due to the incomplete decomposition of the precursor. These limitations can be decreased by controlling the reactions induced by secondary electrons with energy distributions below 100 eV. These electrons are abundant in the surroundings of the interaction electron beam region and therefore contribute with reactions leading to the incomplete decomposition of the precursor. Comparing gas phase dissociative electron attachment with surface studies allows for insight into primary deposition mechanisms for individual precursor [1].

In this communication we will present electron interactions with  $\text{WCl}_6$  [2],  $\text{W}(\text{CO})_6$  [3, 4] and  $\text{Cr}(\text{CO})_6$ . We will address positive and negative ion formation upon low energy electron interactions as well as the differences observed for such FEBID compounds. The experiments have been carried out in the Innsbruck Laboratory by means of double-focusing mass spectrometer in reversed Nier-Johnson geometry.

- [1] R. M. Thorman, R. Kumar T. P., D. H. Fairbrother, O. Ingólfsson, *Beilstein J. Natotechnol.* **6** (2015) 1904.
- [2] M. Neustetter, F. Ferreira da Silva, S. Denifl, *Rapid Commun. Mass Spectrom.* **30** (2016) 1139.
- [3] M. Neustetter, A. Mauracher, P. Limão-Vieira, S. Denifl, *Phys. Chem. Chem. Phys.* (2016) DOI: 10.1039/c6cp00558f.
- [4] K. Wnorowski, M. Stano, C. Matias, S. Denifl, W. Barszczewska, Š. Matejčík, *Rapid Commun. Mass Spectrom.* **26** (2012) 2093.

## Dissociative electron attachment to benzene chromium tricarbonyl

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We have investigated dissociative electron attachment to benzene chromium tricarbonyl ( $M = Cr(C_6H_6)CO_3$ ). This molecule was in our interest because it is a possible Focused Electron Beam Induced Dissociation (FEBID) precursor. Measurements were performed on experimental setup settled in Siedlce, Poland. Incident electron beam with energy resolution of FWHM  $\approx 160$  meV (in the present experiment), orthogonally intersects with the molecular beam resulting in dissociation and formation of fragments. The obtained action tandem mass spectra were performed for the energies from 0 eV to 14 eV, with 2 eV step. The compound showed a very rich fragmentation pattern. We have observed the following fragments:  $[M - (CO)]^-$  ( $m/z$  186),  $[M - (CO)_2]^-$  ( $m/z$  158),  $[M - (CO)_3]^-$  ( $m/z$  130),  $[M - C_6H_6]^-$  ( $m/z$  136),  $Cr^-$  ( $m/z$  52),  $[Cr(CO)_2]^-$  ( $m/z$  108) and  $[Cr(CO)]^-$  ( $m/z$  80). Energy scan was performed for every fragment mentioned above (some anionic yields are shown in Fig.1). Quite high intensity of  $Cr^-$  has been noticed.  $SF_6$  was introduced after every two energy scans, for checking the energy scale calibration.

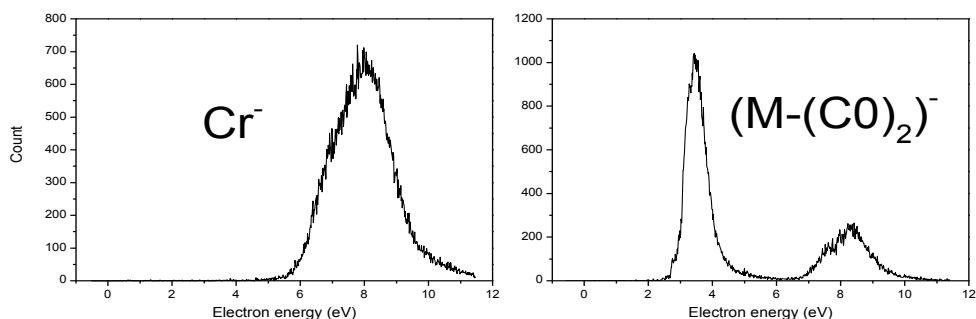


Fig. 1. Ion yield of  $Cr^-$  (52 a.m.u) and  $(M-(CO)_2)^-$  (158 a.m.u) produced from electron impact on gaseous benzene chromium(0) tricarbonyl.

[1] C. Koenig-Lehmann, J. Kopyra, I. Dabkowska, J. Kočišek and E. Illenbergera, *Phys. Chem. Chem. Phys.* **14** (2008) 6954.

## Low-Energy Electron Interaction with Tungsten Hexacarbonyl Clusters

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Low-energy (<100eV) electron interactions with tungsten hexacarbonyl in the gas phase have been reported in the past [1, 2] although we note lack of comprehensive studies in aggregates. Thereby the electron ionization mass spectrum and appearance energies of the most abundant cations were recorded and analyzed, as well as the dissociative electron attachment reactions. Recently we have investigated the interaction of tungsten hexacarbonyl clusters with low-energy electrons utilizing a double focusing two-sector field mass spectrometer [3]. The bare  $W_2^+$  metal cation was observed and a mechanism for the formation of this fragment upon electron impact ionization of the weakly bound  $W(CO)_6$  dimer was proposed: this metal cation can be observed due to fast conversion of the weak cluster bond into a strong covalent bond between the metal moieties. In addition to this finding, further investigations were performed with a setup where an electron beam with high electron energy resolution was crossed with tungsten hexacarbonyl embedded in ultra-cold (0,37K) helium droplets. Cations formed in the ionized droplets were observed with a quadrupole mass spectrometer. A remarkable difference between fragmentation of bare clusters and clusters embedded in helium droplets was found and the formation of tungsten hexacarbonyl dimer is suppressed in helium droplets.

Acknowledgment: This work has been supported by FWF, Wien, Austria (I1015), and the COST Action CM1301 (CELINA).

[1] K. Wnorowski, M. Stano, W. Barszczewska, A. Jówko, Š. Matejčík, *Int. J. Mass Spectrom.*, **42**, (2012) 314.

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

[3] M. Neustetter, A. Mauracher, P. Limão-Vieira, S. Denifl, *Phys. Chem. Chem. Phys.* (2016)

DOI: 10.1039/C6CP00558.

## Introduction to Atomic Layer Deposition and the COST Action HERALD

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Atomic layer deposition (ALD) is a unique technique for growing ultra-thin films that is enabling new developments in high-tech manufacturing sectors such as electronics, energy and coatings. With interest growing worldwide, the time is right to coordinate European activity in this field. HERALD (COST action MP1402) aims to structure and integrate European research activity in ALD, bringing together existing groups, promoting young scientists and reaching out to industry and the public. HERALD supports collaboration through lab visits, workshops and training schools.

As Chair of HERALD, I will present a general introduction to ALD and will mention areas where it has been combined with EBID to achieve patterning and selective area deposition [1]. I will give a brief overview of my own research in the atomic-scale modelling of ALD mechanism [2-4] and suggest how this could contribute to EBID.

[1] A. J. M. Mackus, N. F. W. Thissen, J. J. L. Mulders, P. H. F. Trompenaars, M. A. Verheijen, A. A. Bol, W. M. M. Kessels, *J. Phys. Chem. C* **117** (2013) 10788.

[2] S. D. Elliott, G. Dey, Y. Maimaiti, H. Ablat, E. A. Filatova, G. N. Fomengia, *Adv. Mater.* (2015) DOI 10.1002/adma.201504043

[3] H. Pedersen, S. D. Elliott, *Theor. Chem. Acc.* **133** (2014) 1476.

[4] S. D. Elliott, *Semicond. Sci. Technol.* **27** (2012) 74008.



## Nanopore Fabrication and Characterization by Helium Ion Microscopy

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The helium ion microscope (HIM) is a charged particle microscope that utilizes helium ions for probing of a sample. In the low dose regime, the HIM operates as microscope, high doses enable material modification and sputtering. Compared to conventional focused ion beams (FIB) using metal ions like gallium, the HIM offers a very small focal spot size down to 0.35 nm and a strongly localized sputter interaction with the material. We employ the HIM for both milling nanopores in free-standing membranes as well as for the inspection of nanopores. The helium ion beam with its unique properties overcomes the resolution limit of conventional FIB tools as we show in a comparison with a high resolution gallium FIB. We investigated three different materials: 30 nm thick silicon nitride, graphene and 1 nm thick carbon nanomembranes (CNM) made from aromatic self-assembled monolayers by electron-induced cross-linking. By HIM milling and imaging we can detect smallest nanopores at 3 nm diameter in all membranes. Further studies on CNM with an atomic resolution scanning transmission electron microscope (STEM) revealed even nanopores with diameters of less than 2 nm made by ion beam exposure.

Different strategies for milling and characterizing pores with HIM will be discussed. In particular, we demonstrate two approaches of creating nanopores into membranes of different materials. One approach allows to control the aspect ratio of the pores while the other approach yields smaller diameters. A comparison about the feasibility of different characterization methods includes the ion generated secondary electron signal of HIM, the He<sup>+</sup> transmission signal as well as STEM. Sputter yield values for the investigated membrane types and the He<sup>+</sup> beam profile were obtained from dose-dependent nanopore diameters.

## Electron beam processes for surface functionalization and directed nanostructure assembly

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Electron beam induced irradiation in precursor gases such as water and ammonia has been used extensively for purification and etching of electron beam deposited materials and other nanostructures. Here, we discuss two novel applications of electron beam induced etching (EBIE) for fabrication of photonics, plasmonics and sensing devices. First, we demonstrate high resolution etching of hBN mono and multilayers by a non-destructive electron beam induced etching (EBIE) process using H<sub>2</sub>O as the reactive gas. In the EBIE process, the chemical reaction is highly localized to the electron beam irradiated area, allowing for room temperature direct write fabrication of complex patterns with nanoscale resolution. We employ our unique etching technique to fabricate boron nitride nanoribbons, which are of particular interest due to their predicted new electromagnetic and optoelectronic properties. Unlike prior studies of the modification of 2D materials using high energy electron irradiation in transmission electron microscopes, the low energy H<sub>2</sub>O-mediated etch process leaves the surrounding hBN material unmodified and contamination-free. This demonstration of a nondestructive technique for fabrication of boron nitride nanostructures with user-defined anisotropic edge geometries will open up a range of applications in fabrication of new 2D heterostructures and devices.

We also show that the ammonia-mediated EBIE process can be adapted to enable high-resolution surface functionalization for directed assembly of nanostructures such as nanodiamonds and colloidal quantum dots. Such directed assembly of metal nanoparticles and fluorescent nanoparticles is required for many applications spanning sensing, photonics, plasmonics and quantum information. We demonstrate that beam directed amine functionalization can be used to initiate covalent bonding of nanostructures such as nanodiamonds and gold colloids to selected regions of the sample. This assembly method offers extremely high yield (>92%), 100% selectivity, and unprecedented stability, which we demonstrate by subjecting fabricated nanodiamond arrays to multiple sonication steps of up to 12 hours total duration.

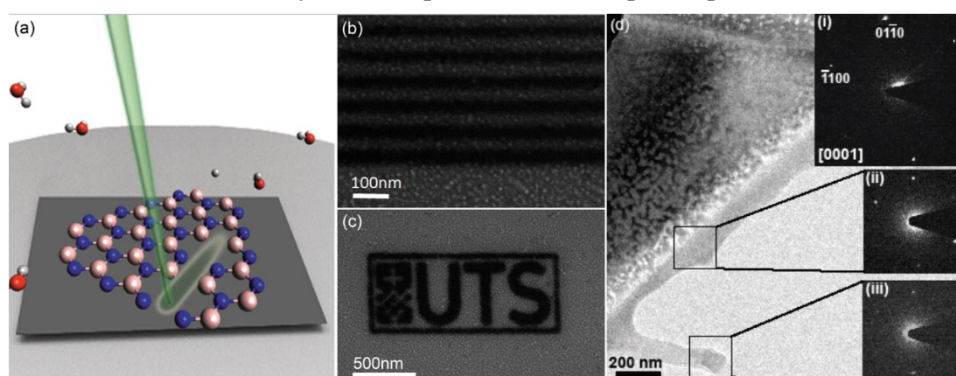


Fig. 1. (a) Schematic of the electron beam induced etching process of hBN using H<sub>2</sub>O. (b), (c) EBIE patterns in multilayer hBN. (d) TEM image of an etch region on exfoliated hBN flake (i) SAED pattern from pristine hBN region (ii), (iii) SAED pattern from denoted square.

**Michael Allan - electron impact spectroscopy at its best**

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## Resonances and Threshold Effects in Electron Collisions with Molecules and Clusters

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This talk will reflect on our work with Michael Allan on resonances and threshold effects in inelastic electron collisions with molecules. We were interested in threshold structures controlled by the long-range electron-molecule interaction, dipolar and polarization. Particularly interesting examples are vibrational excitation and electron attachment processes in electron collisions with HF[1], CH<sub>3</sub>I[2] and SF<sub>6</sub>[3] molecules. An important feature of experimentally observed threshold structures is that they contain information about the mechanisms for inelastic processes. In particular Allan was first to suggest [4] that electron impact vibration excitation of the O-H stretch in the formic acid is driven by a  $\sigma^*$  resonance similar to what happens in hydrogen halides [1]. This inspired our group at the University of Nebraska to proceed with dissociative electron attachment calculations [5] involving formation of a very broad  $\sigma^*$  resonance. Our result led to a debate [6,7] which was resolved by the Allan group measurements [8] confirming the  $\sigma^*$  mechanism. We showed later that this mechanism is operable in other biologically relevant molecules.

Michael Allan's work [9] on near-threshold vibrational excitation of the CO<sub>2</sub> molecule inspired us (together with Hartmut Hotop) to study low-energy electron attachment to van der Waals CO<sub>2</sub> clusters [10]. This process is strongly dominated by vibrational Feshbach resonances. The strong selectivity in excitation of individual components of the Fermi dyad, observed by Allan, is suppressed in the case of clusters. This and several other interesting physics results will be reviewed in the talk.

Acknowledgments: This work has been supported by the US National Science Foundation. In addition to Michael Allan's contribution, I acknowledge fruitful collaborations with Hartmut Hotop, Martin Ruf, Paul Burrow, Gordon Gallup, and Jiri Horacek.

- [1] M. Cizek, J. Horacek, M. Allan, I. I. Fabrikant, and W. Domcke, *J. Phys. B* **36** (2003) 2837.
- [2] M. Allan and I. I. Fabrikant, *J. Phys. B* **35** (2002) 1025.
- [3] I. I. Fabrikant, H. Hotop, and M. Allan, *Phys. Rev. A* **71** (2005) 022712.
- [4] M. Allan, *J. Phys. B* **39** (2006) 2939.
- [5] G. A. Gallup, P. D. Burrow, and I. I. Fabrikant, *Phys. Rev. A* **79** (2009) 042701.
- [6] T. N. Rescigno, C. S. Trevisan, and A. E. Orel, *Phys. Rev. A* **80** (2009) 046701.
- [7] G. A. Gallup, P. D. Burrow, and I. I. Fabrikant, *Phys. Rev. A* **80** (2009) 046702.
- [8] R. Janeckova, D. Kubala, O. May, J. Fedor, and M. Allan, *Phys. Rev. Lett.* **111** (2013) 213201.
- [9] M. Allan, *Phys. Rev. Lett.* **87** (2001) 033201.
- [10] I. I. Fabrikant and H. Hotop, *Phys. Rev. Lett.* **94** (2005) 063201.

## Negative ion resonances of polyatomic molecules: are they relevant for search of FEBID precursors?

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We will present two theoretical approaches that allow us to look for the negative ion resonances that may drive the DEA process for FEBID precursors. The first approach is based on scattering calculations of vibrational Electron Energy-Loss Spectra (EELS) by employing the Discrete Momentum Representation (DMR) method [1]. The second procedure involves quantum chemistry calculations of the electron affinities in the presence of an attractive external field. The field-dependent affinities are then analytically continued to the zero field conditions by use of Regularized Analytic Continuation (RAC) method [2]. This technique allows accurate extraction of the resonance position and width for low-energy collisions. Strong points, but also limitations of the presented methods will be discussed.

[1] R. Čurík, I. Paidarová, M. Allan and P. Čársky, *J. Phys. Chem. A*, **118** (2014) 9734.

[2] J. Horáček, I. Paidarová, R. Čurík, *J. Chem. Phys.* **143** (2015) 184102.

## Cluster-beam experiments and the insight they bring into FEBID

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We present a detailed study of electron-induced processes in iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , that is in an elementary degree of aggregation – in form of cryogenic clusters. We have two ways of preparing such clusters: either co-expanding the precursor molecules with buffer gas, thus creating aggregates of pure precursor, or picking up multiple precursors on a surface of large argon clusters (hundreds of Ar atoms) and thus creating precursor aggregates on a 'nanosupport' [1]. The first way has been probed independently on two setups (in Prague and in Bratislava) and the results are in an excellent agreement.

The measurements of negative ion yields in both cases show that while anions containing one iron atom show strong resonances at very low electron energies, the yields of more complex anions show broad bands at electron energies above 5 eV. Based on comparison with the electron-energy loss spectra of  $\text{Fe}(\text{CO})_5$  we postulate a two-center process that involves electronic excitation of one aggregate constituent and attachment of electron with low residual energy to another aggregate constituent (*self-scavenging*). The dimer anion formation appears to completely determine the aggregation of larger complexes. Clear differences appear in pure aggregates of  $\text{Fe}(\text{CO})_5$  when compared to those supported by argon nanoparticles. We explain these differences on the basis of different excitation and relaxation pathways of the singlet and triplet states of  $\text{Fe}(\text{CO})_5$  in the initial stage of self-scavenging.

Acknowledgments: This work has been supported by the COST action CM1301 CELINA, Czech Science Foundation projects Nr. 16-10995Y and 15-102386S, Slovak Grant Agency VEGA 1/0417/15 and Slovak Research and Development Agency project Nr. APVV-0733-11.

[1] J. Lengyel, J. Kočišek, M. Fárník, J. Fedor, *J. Phys. Chem. C* **120** (2016) 7397.

## FEBID nanolithography for the realization of fundamental thought experiments

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Two fundamental thought experiments proposed in the 50s and 60s have been realized with the original schemes by means of FEBID and FIB nanofabrication. The first experiment (Fig. 1(a)), suggested by Feynman in his famous lectures [1], is the interference and diffraction of electrons through nanoslits, which we have realized by opening two nanoslits on a silicon nitride membrane by FIB milling to obtain interference of 200 keV electrons in a TEM, and then closing one by FEBID to obtain single-slit diffraction [2]. The second experiment is the detection of the Ehrenberg-Siday effect, whereby the phase of electrons is modified by traveling in a zero magnetic field region ( $B=0$ ) with non-zero magnetic flux ( $\Phi \neq 0$ ) [3]. Starting from the same two-nanoslits setup (Fig. 1(b)), the experiment was realized by FEBID of a Co nanobar in between the slits, and observation of the shift in the interference figure as the bar magnetization was changed [4]. These experiments demonstrate the great flexibility of FEBID nanolithography especially when performed in a Dual Beam FIB-SEM apparatus.

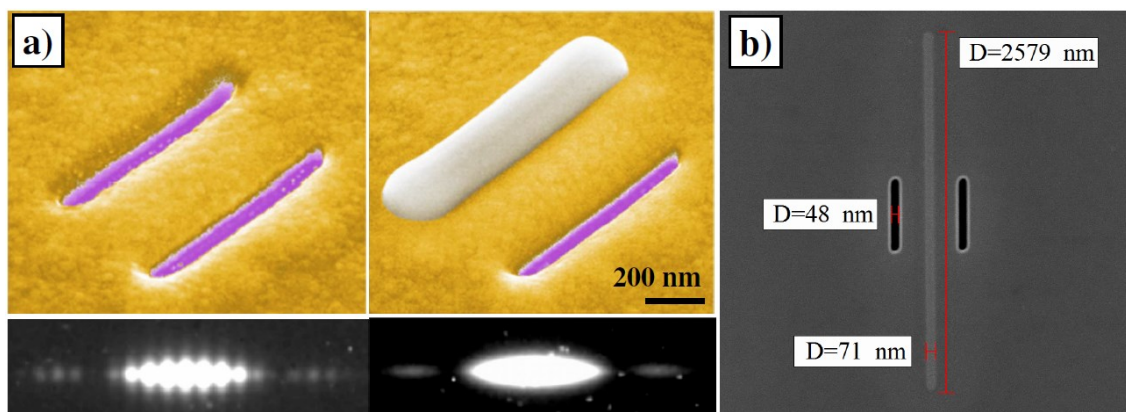


Fig. 1. (a) Interference (left) and diffraction (right) of electrons through nanoslits. (b) FEBID Co nanobar between nanoslits for the Ehrenberg-Siday experiment.

[1] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, MA, 1966), Vol. 3, Chap. 1

[2] S. Frabboni, G. C. Gazzadi and G. Pozzi, *Appl. Phys. Lett.* **93** (2008) 073108.

[3] W. Ehrenberg and R. E. Siday, *Proc. Phys. Soc., Sec. B* **62** (1949) 8.

[4] G. Pozzi et al., *Appl. Phys. Lett.* **108** (2016) 083108.



## Gas-assisted electron-beam-induced nanopatterning of high-quality titanium oxide

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A variety of applications require nanoscale patterns of a high quality insulator. One such application is magnetic tunnel junctions. Silicon oxide, which has an established electron beam induced deposition (EBID) process for obtaining high purity patterns, does not appear to be suitable for this particular application due to inter-diffusion of Co into silicon oxide at elevated temperatures [1]. Thus a different material is needed.

Among the large number of metal oxide materials, titanium dioxide (TiO<sub>2</sub>) is one of the most versatile. The range of applications extends from cosmetics to gas sensing, photovoltaics and photocatalysis. We describe EBID of titanium oxide nanopatterns. The precursor is titanium tetraisopropoxide, delivered to the deposition point through a needle and mixed with oxygen at the same point via a flow through a separate needle. The depositions are free of residual carbon and have an EDX determined stoichiometry of TiO<sub>2.2</sub> [2].

High resolution transmission electron microscopy and Raman spectroscopy studies reveal an amorphous structure of the fabricated titanium oxide. Ellipsometric characterization of the deposited material shows a refractive index of 2.2–2.4 RIU in the spectral range of 500–1700 nm and a very low extinction coefficient (lower than 10<sup>-6</sup> in the range of 400–1700 nm), which is consistent with high quality titanium oxide. The electrical resistivity of the titanium oxide patterned with this new process is in the range of 10–40 GΩ cm and the measured breakdown field is in the range of 10–70 V μm<sup>-1</sup>. The fabricated nanopatterns are important for a variety of applications, including field-effect transistors, memory devices, MEMS, waveguide structures, bio- and chemical sensors.

[1] B. N. Costanzi, A. V. Riazanova, E. D. Dahlberg, and L. M. Belova, *Appl. Phys. Lett.* **104** (2014) 222401.

[2] A V Riazanova, B N Costanzi, A I Aristov, Y G M Rikers, J J L Mulders, A V Kabashin, E Dan Dahlberg and L M Belova, *Nanotechnology* **27** (2016) 115304.

## Argon mediated ionization of Fe(CO)<sub>5</sub> molecules deposited on argon nanoparticles

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In order to understand the effect of environment, we have recently performed a series of experiments on the Fe(CO)<sub>5</sub> molecules deposited on argon nanoparticles using reflectron time-of-flight mass spectrometer with variable electron energy ionization source. The doped nanoparticles are interacted with an electron beam of 0-70 eV and they are ionized either negatively by electron attachment or positively by electron impact ionization. Negative nanoparticle analysis [1] is presented in a separate contribution.

In this contribution we focus on the positive ion analysis. We have measure the electron energy dependent ion yields. A significant difference in appearance energies (AE) of Fe(CO)<sub>5</sub> ion fragments on Ar nanoparticles in comparison to its isolated form was observed. The AEs of different fragments from isolated molecules depend on the number of CO ligands [2]. On the other hand, all the observed ion fragments in the doped nanoparticles are produced at the same energy around 15 eV that significantly higher than the ionization potential of Fe(CO)<sub>5</sub> molecule starting from 8.5 eV. The observed shift in AE values demonstrates the effect of the “*inert*” argon environment on the electron induced process of Fe(CO)<sub>5</sub> molecule that will be discussed.

Acknowledgments: Funding by the Lise Meitner Programm of the Austrian Science Fund (FWF) project No. M1983-N34, by the Czech Science Foundation project No. 14-08937S and by the CELINA COST Action CM1301 is gratefully acknowledged.

[1] J. Lengyel, J. Kočíšek, M. Fárník, J. Fedor, *J. Phys. Chem. C* ASAP (2016) DOI: 10.1021/acs.jpcc.6b00901.

[2] M. Lacko, P. Papp, K. Wnorowski, Š. Matejíček, *Eur. J. Phys. D* **69** (2015) 82.

## Excited States of Pt(PF<sub>3</sub>)<sub>4</sub> and Their Role in Focused Electron-Beam Nanofabrication

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Electron-induced chemistry of metal-containing molecules is central in focused electron beam induced deposition (FEBID). While some elementary processes leading to precursor decomposition were quantitatively characterized, *e.g.* electronic excitation by electron impact [1], dissociative electron attachment (DEA) [2], electron-induced chemistry on the surfaces [3], data for neutral dissociation (ND) are missing. Here we provide an indication of how important is the ND channel in the model precursor Pt(PF<sub>3</sub>)<sub>4</sub>, tetrakis(trifluorophosphine)platinum(0).

We have utilized the density functional and time-dependent density functional theory based approaches to characterize ground and excited states for the Pt(PF<sub>3</sub>)<sub>4</sub>. The calculations revealed a number of phenomena, related to the nature of Pt-P bond, that can play a role in the electron-induced chemistry of this compound, *e.g.* a considerable increase of bond dissociation energy with a sequential removal of multiple ligands. The calculated electronically excited states were validated by the comparison with electron energy loss spectra [1]. From the shape of the potential energy curves, it is concluded that the lowest excited states are dissociative, either directly or, via conical intersections. Taking into account typical electron energy distribution at the FEBID spot reveals that the importance of ND exceeds that of DEA in Pt(PF<sub>3</sub>)<sub>4</sub>. We thus established neutral dissociation as an important, albeit largely neglected, channel for FEBID using Pt(PF<sub>3</sub>)<sub>4</sub> as a precursor. This conclusion is likely to apply to other precursors as well.

[1] M. Allan, *J. Chem. Phys.* **134** (2011) 204309.

[2] O. May, D. Kubala, M. Allan, *Phys. Chem. Chem. Phys.* **14** (2012) 2979.

[3] K. Landheer, S. G. Rosenberg, L. Bernau, P. Swiderek, I. Utke, C. W. Hagen, D. H. Fairbrother, *J. Phys. Chem. C* **115** (2011) 17452.

## Introduction to atomic layer deposition (ALD) and its links with FEBIP

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Atomic layer deposition (ALD) [1] is a vapor phase deposition technique that has gained a tremendous amount of attention in the recent years. The reason is that it allows for the deposition of ultrathin films of high quality with a very accurate control of the thickness. Moreover, the method is unique in its ability to cover demanding surface topologies (e.g., substrates with deep trenches) with very conformal films having the same thickness everywhere. The method has therefore become a real enabling technology in the semiconductor industry but applications in other fields of technology are rapidly expanding.

In this presentation, I will (i) give an introduction into ALD; (ii) describe its similarities to focused electron beam induced processes (FEBIP) – for example, in terms of precursor requirements and precursor choices – and (iii) show how FEBIP and ALD can be combined to realize an interesting process for nanopatterning [2, 3].

[1] H.C.M. Knoop, S.E. Potts, A.A. Bol, and W.M.M. Kessels, *Handbook of Crystal Growth*, Vol. III (eds. T. Nishinaga, T.F. Kuech). Elsevier (2015) 1101.

[2] A.J.M. Mackus, S.A.F. Dielissen, J.J.L. Mulders, W.M.M. Kessels, *Nanoscale* **4** (2012) 4477.

[3] A.J.M. Mackus, A.A. Bol W.M.M. Kessels, *Nanoscale* **6** (2014) 10941.

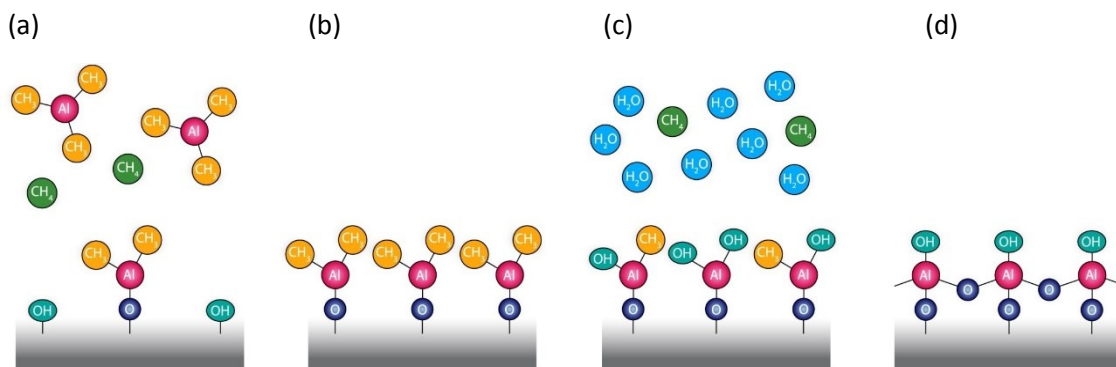


Fig. 1. Schematic representation of the prototypical ALD process of Al<sub>2</sub>O<sub>3</sub>: (a) precursor (Al(CH<sub>3</sub>)<sub>3</sub>) dosing; (b) purge; (c) co-reactant (H<sub>2</sub>O) dosing; and (d) purge. The temperature window for ALD processes lies typically in the range 100 – 400 °C.

## Combined top-down and bottom-up 3D nanofabrication

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Electron Beam Induced Deposition (EBID) is an attractive nanofabrication technique offering high resolution, versatility in materials deposited and ease of implementation in a commercial SEM. To exploit its potential for high resolution lithography, however, requires control over several aspects not studied in detail so far. Major advancement as regards reproducibility of EBID lines, metrology, process control and 3D line profile are needed for its development as an alternative lithography technique. Further to the demonstration of high resolution on bulk silicon [1], we identified a regime in which reproducible patterning can be carried out regardless of patterning strategy [2]. Sub-30 nm dense EBID lines have been fabricated in this regime and the line width and line edge roughness were measured using a newly developed edge detection technique. The advantages and limitations of secondary and backscattered electron (SE and BSE) imaging for metrology are discussed in the context of these lines. Subsequent to this characterization, the reproducibility of the lines has been measured and found to be quite high. The line width is reproducible to within 3 nm and the line edge roughness is quite low ( $1\sigma$  value  $< 1.5$  nm), making it a competitive lithography technique where EBL is the state of the art. A process has been developed to enable the fabrication of lines of desired width, taking into account proximity effects as a function of line spacing. And finally, the 3D line profile in this regime has been studied using FIB sectioning. A Gaussian shape with long tails is observed as a consequence of the deposition being initiated not only by the primary electrons but by SE's and BSE's as well. This is a problem in the fabrication of dense lines, introducing unwanted material and crosstalk. A complementary top-down technique called Electron Beam Induced Etching (EBIE) has been used in combination with EBID to modify the line profile. A simple analytical model has been developed to study the sidewall evolution, followed by experiments resulting in the fabrication of EBID structures with vertical sidewalls.

[1] J. C. van Oven, F. Berwald, K. K. Berggren, P. Kruit, C. W. Hagen, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, **29** (2011)06F305.

[2] S. Hari, C. W. Hagen, T. Verduin, and P. Kruit, *J. Micro/Nanolithography, MEMS, MOEMS* **13** (2014) 033002.

## Fabrication of carbon nanostructures on metal deposits prepared by EBID

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Carbon Nanotube (CNT) is the material lying between fullerenes and graphite as a new member of carbon allotropes. Based on their unique properties (high thermal-, electrical conductivity, very high tensile strength and highly flexible) the CNTs can be used in micro- and nano-electronics, catalyst, gas storage. Single-wall or multi-wall carbon nanotubes can be prepared by catalytic chemical vapour deposition (CCVD) [1]. In the present study, metal nanoparticles (e.g. Fe, Co) were employed as catalyst for the growth of the CNTs.

Electron beam induced deposition (EBID) is an excellent method to prepare nanosized metal-containing particles [2]. In our ultra-high vacuum setup we can divide this nano-structuring process in two steps: the first part is the deposition of the non-volatile dissociation products of the precursors by the impact of the electron beam. Here we are able to control the lateral position and to some extent the size of the metal nanostructures. The second part is autocatalytic growth of the metal particles. In this step we are able to control the corresponding enlargement of the patterns and increase the purity of metal particles [3].

By combining a CCVD method for the growth of the CNTs with the EBID process, we envision to fabricate carbon nanotubes at predefined positions with controlled diameter and length. Proof of principle, i.e., the selective growth of carbon nanostructures at the position of the metallic EBID deposits, will be presented and discussed.

[1] Z. Kónya *Carbon Filaments and Nanotubes: common origins, differing applications?* Dordrecht: Kluwer Academic Publishers, (2001). 85-109.

[2] a) W.F. van Dorp, C.W. Hagen, *J. Appl. Phys.* **104** (2008) 081301; b) Utke, et al., *JVST B* **26**, (2008) 1197; c) S. J. Randolph et al., *Crit. Rev. Solid State Mater. Sci.* **31** (2006) 55.

[3] H. Marbach, *Appl. Phys. A*, **117** (2014) 987.

## Granular metals prepared by FEBID from copper and gold metalorganic precursors for gas-sensing applications

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In this work we present results of gas-sensing studies of granular systems, obtained by FEBID from gold and copper metalorganic precursors. The deposited structures were thermally postannealed in vacuum in order to start the formation of metallic nanocrystals. The process for  $\text{Cu}(\text{hfac})_2$  precursor was already described in [1]. Those kinds of systems could be potentially used for gas-sensing due to their internal structure – metallic grains embedded in a low conductive matrix. The application of Pt-C FEBID deposits towards the humidity sensing, based on the nanogranular microstructure was shown and explained in [2]. Our studies are focused on searching for other materials, possessing similar properties, obtained from separate and simultaneous injection of  $\text{Cu}(\text{hfac})_2$  and  $\text{Me}_2(\text{Au})\text{acac}$  precursors. The deposited FEBID structures were further postannealed in vacuum and investigated by Energy Dispersive X-ray spectroscopy, Raman spectroscopy, Atomic Force Microscopy and High Resolution Scanning Electron Microscopy.

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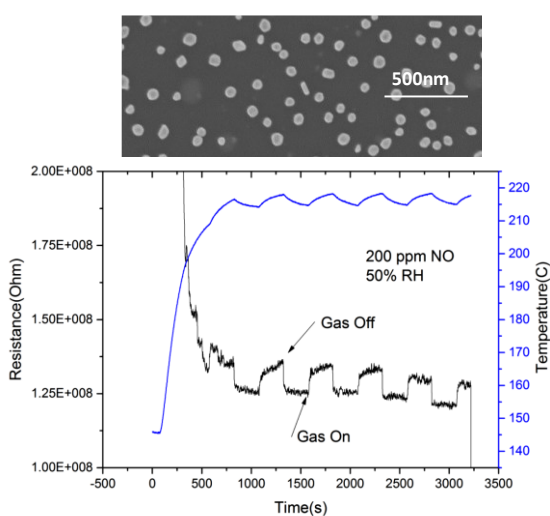


Fig. 1: Gas sensing response to NO of Cu-C FEBID deposit microstructure after postannealing in vacuum to 200°C: SEM images of the deposit microstructure (top) gas-sensing response to NO.

[1] A. Szkudlarek, A. Rodrigues Vaz, Y. Zhang, A. Rudkowski, C. Kapusta, R. Erni, S. Moshkalev, I. Utke, *Beilstein J. Nanotechnol.*, **6** (2015) 1508

[2] M. Huth, F. Kolb, H. Plank, *Appl. Phys. A* **117** (2014) 1689.

## Molecular Dynamics for Irradiation Driven Chemistry: Application to the FEBID process

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A new molecular dynamics (MD) approach for computer simulations of irradiation driven chemical transformations of complex molecular systems is suggested. The approach is based on the fact that irradiation induced quantum transformations can often be treated as random, fast and local processes involving small molecules or molecular fragments. We advocate that the quantum transformations, such as molecular bond breaks, creation and annihilation of dangling bonds, electronic charge redistributions, changes in molecular topologies, etc, could be incorporated locally into the molecular force fields that describe the classical MD of complex molecular systems under irradiation. The proposed irradiation driven molecular dynamics (IDMD) methodology is designed for the molecular level description of the irradiation driven chemistry.

The IDMD approach is implemented into the MBN Explorer software package [1] capable to operate with a large library of classical potentials, many-body force fields and their combinations. IDMD opens a broad range of possibilities for modelling of irradiation driven modifications and chemistry of complex molecular systems ranging from radiotherapy cancer treatments to the modern technologies such as focused electron beam deposition (FEBID).

As an example, the new methodology is applied for studying the irradiation driven chemistry caused by FEBID of tungsten hexacarbonyl -  $W(CO)_6$  precursor molecules on a hydroxylated  $SiO_2$  surface. It is demonstrated that knowing the interaction parameters for the fragments of the molecular system arising in the course of irradiation one can reproduce reasonably well experimental observations and make predictions about the morphology and molecular composition of nanostructures that emerge on the surface during the FEBID process.

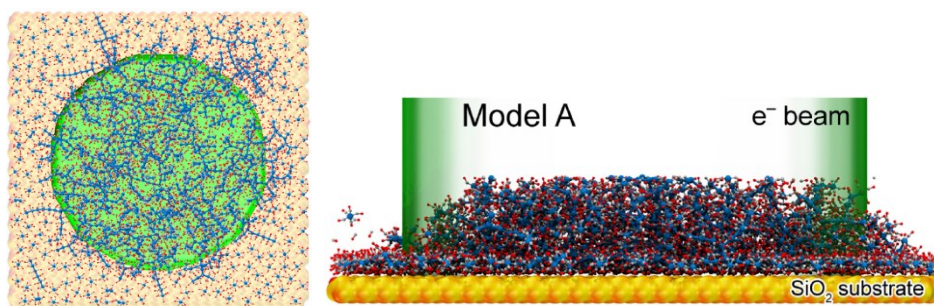


Fig. 1. Example of the IDMD simulation of W enriched nanostructure (left- top view, right- side view) atop the hydroxylated  $SiO_2$  surface created in the FEBID process of  $W(CO)_6$  precursors.

[1] I.A. Solov'yov, A.V. Yakubovich, P.V. Nikolaev, I. Volkovets, A.V. Solov'yov, *J.Comp.Chem.* **33** (2012), 2412. [www.mbnexplorer.com](http://www.mbnexplorer.com); [mbnresearch.com](http://mbnresearch.com)



## Focused electron beam induced surface reactions - from surface termination to etching

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Focused electron beam induced processing (FEBIP) uses controlled scanning of a focused electron beam to directly deposit (FEBID) or to directly etch (FEBIE) nanostructures. During etching, an initial delay has been experienced before material removal sets in. In couple of cases, this might be related to the oxide surface of the material. Nevertheless, no clear explanation has been provided so far. We have investigated the FEBIP process using chlorine as an etch gas. This work will demonstrate that chlorine surface reaction occurs even before the geometrical changes can be seen.

To track this process, we mainly use electrical characterization of semiconductor (Silicon and Germanium) test device and surface analysis studies using AFM, EDX and TEM. LEO 1540 VP Scanning Electron Microscope (SEM) has been used to activate precursor's molecules. Chlorine is inserted inside the chamber through a custom-built gas injections system with a fixed flow of 0.13 sccm. An acceleration voltage of 5 kV with high current mode and beam current of 1 nA and 5 nA were used during the etching procedure.

The entire process can be distinguished in two different regimes. Firstly, in case of small/short exposure of chlorine with electron beam, surface analysis studies indicate that the chlorine reacts with the surface of the semiconductor while no sufficient formation of volatile silicon chloride sets in, which means that no material is removed. Secondly, etching is observed only after long term exposure to the electron beam.

In this study we mainly focus on chlorine termination of the surface induced by electron irradiation. Chlorine alone didn't change the electrical resistivity, rather it undergoes a spontaneous reaction with silicon. Also, electron beam alone didn't change anything, no or negligible effect of residual gas deposits. There was no effect observed on recrystallization of the material due to electron beam heating. Only if the chlorine and electron beam activated together, the change in the surface was detected. In case of flat crystalline plane, slower etching rate was observed and vice-versa.

While deposition and etching have received wide focus among the research community, the initial phases of those processes have many question marks - what happens to surface for short term exposure and how does this change the substrate is still remain an open field which needs to be investigated.

- [1] M.M. Shawrav, Z.G. Gökdeniz, H.D. Wanzenboeck, P. Taus, J.K. Mika, S. Waid, E. Bertagnolli, *Mat Sci. in Semi.* **42** (2016) 170.
- [2] P. Roediger, M. Mijic, C. Zeiner, A. Lugstein, H.D. Wanzenboeck, E. Bertagnolli, *J. Vac. Sci. Technol. B.* **29** (2011) 06FB03.
- [3] P. Roediger, H.D. Wanzenboeck, G. Hochleitner, E. Bertagnolli, *J. Vac. Sci. Technol. B* **29** (2011) 041801.

## Application of tailored metal-organic precursors in Focused Electron Beam Induced Deposition (FEBID) of Iron Oxides (FeO<sub>x</sub>): Fe(tbaoac)<sub>3</sub> and Fe(pki)<sub>2</sub>

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(Focused electron) beam induced deposition ((FE)BID) is gaining intense attention from the materials research society due to its unique features, such as localized nanostructuring of advanced materials and nanoscale device fabrication. Although this technique has been established since the early 1990s, one major drawback of FEBID is the incorporation of precursor residuals within the nanostructures. For BID of FeO<sub>x</sub> only very few iron containing precursors have been applied. Typically iron carbonyls, such as Fe(CO)<sub>5</sub> [1], were employed as iron source, very few reports are also available on the application of [Fe(III) 2-ethyl hexanoate]<sub>n</sub>[2] and Ferrocene[3]. Surprisingly, there are dozens of iron containing compounds known, which are applied in different vapor phase methods relying on the decomposition of precursors (e.g. chemical vapor deposition), whereupon iron (III) *tert*-butyl acetoacetate [Fe(tbaoac)<sub>3</sub>] and iron (II) isopropyl ketoiminate [Fe(pki)<sub>2</sub>] were successfully applied in MOCVD processes resulting in high quality iron oxide thin films [4]. Therefore, both [Fe(tbaoac)<sub>3</sub>] and [Fe(pki)<sub>2</sub>] were evaluated for FEBID of iron deposits. A heated external reservoir connected to a carrier gas system was applied for the precursor transport. Furthermore, the nanostructures obtained with [Fe(pki)<sub>2</sub>] were thoroughly investigated in terms of composition and structure with respect to the set carrier gas flow rate (N<sub>2</sub>) by means of EDX, SEM, and AFM.

[1] M. Gavagnin, H. D. Wanzenboeck, D. Belić, E. Bertagnolli, *ACS Nano* **7** (2012) 777.

[2] S. Trudel, R. H. Hill, *Can. J. Chem.* **87** (2009) 217.

[3] S. W. Chee, R. Sharma, *Micron*, **43** (2012) 1181.

[4] D. Peeters, G. Carraro, C. Maccato, H.Parala, A. Gasparotto, D. Barreca, C. Sada, K. Kartaschew, M. Havenith, D. Rogalla, H.-W. Becker, A. Devi, *Phys. Status Solidi A* **211** (2014) 316.

## Design and performance of an instrument for gas phase electron spectroscopy of trapped molecular ions

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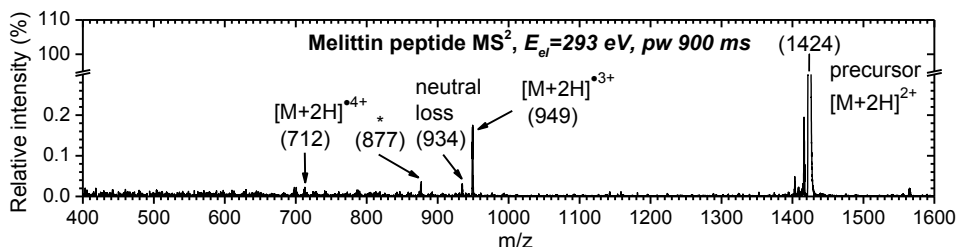
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The electron interaction with atoms and molecules in the gas phase, has been studied for more than a century [1]. Over the years, electrons are used to probe the fundamental properties of atoms and molecules, such as electronic structure and chemical reactivity. Particularly, inner-shell electron spectroscopy of gas phase molecules, found its application in a wide area of research fields [2].

Recently we have designed a new experimental setup [3], for electron impact tandem mass spectrometry and action spectroscopy of electrosprayed macromolecules, by coupling a focused electron gun with a commercial linear ion trap mass spectrometer. Herein, we discuss the experimental details of this setup and the electron beam tracing simulations performed in SIMION to investigate the propagation of 300 eV energy electrons inside the RF linear quadrupole ion trap. We present the first results of electron-induced dissociation of peptides, as well as possibilities to probe trapped CELINA precursor SiOEt<sub>4</sub> by electron impact.



- [1] N. J. Mason, *J. Phys. Conf. Ser.*, **565** (2014) 012001.
- [2] A. P. Hitchcock, *J. Electron Spectros. Relat. Phenomena*, **112** (2000) 9.
- [3] M. Lj. Ranković, A. Giuliani, A. R. Milosavljević, *Appl. Phys. Lett.*, **108** (2016) 064101.

# **Poster contributions**

P-1.	<p><b>On the Puzzling Mechanism of loss of H-Atom in Acidic Compounds: Phenol</b>  <u>Michael Allan</u>  Department of Chemistry, University of Fribourg, Chemin du Musée 9,  Fribourg, Switzerland</p>
P-2.	<p><b>Two-Dimensional Electron Energy Loss Spectra as a Probe of Fast Dynamics in Resonances</b>  <u>Michael Allan</u>  Department of Chemistry, University of Fribourg, chemin du Musée 9,  Fribourg, Switzerland</p>
P-3.	<p><b>Electrons and Ionic Liquids</b>  <u>Michael Allan</u>  Department of Chemistry, University of Fribourg, chemin du Musée 9,  Fribourg, Switzerland</p>
P-4.	<p><b>FIB/SEM electron tomography and 3D reconstruction of solid oxide fuel cell porous anode</b>  <u>Katarzyna Berent</u>  Academic Centre for Materials and nanotechnology, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland</p>
P-5.	<p><b>Theory in Service of CELINA</b>  <u>Petr Čársky</u>  J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic</p>
P-6.	<p><b>Quantum chemical characterization of dopamine</b>  <u>Iwona Dąbkowska</u>  Department of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-936 Poland</p>
P-7.	<p><b>Electron induced fluorescence of acetylene</b>  <u>Michal Ďurian</u>  Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, Bratislava Slovakia,</p>
P-8.	<p><b>Electron-Driven Proton Transfer in Hydrogen-Bonded Systems</b>  <u>Maciej Gutowski</u>  Institute of Chemical Sciences, Heriot-Watt University, Edinburgh EH14 4AS</p>
P-9.	<p><b>Magnetic properties of electrodeposited Pt-CoPt nanowire arrays</b>  <u>Katarzyna Hnida</u>  Academic Centre for Materials and nanotechnology, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow</p>
P-10.	<p><b>Low-energy electron interactions with chromium hexacarbonyl</b>  <u>J. Khreis</u>  Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria</p>

P-11.	<p><b>Radiation reduced CNM formation from halogenated biphenylthiols</b>  <u>S. Koch</u>  Department of Physics, Universität Bielefeld, Universitätsstrasse 25, 33615 Bielefeld, Germany</p>
P-12.	<p><b>Gas sensing properties of CuO/Fe<sub>2</sub>O<sub>3</sub> heterostructures</b>  <u>Kamila Kollbek</u>  Academic Centre for Materials and nanotechnology, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland</p>
P-13.	<p><b>Reactions driven in chloro(dimethyl sulfide)gold(I) by low energy electrons</b>  <u>Janina Kopyra</u>  Siedlce University, Faculty of Sciences, 3 Maja 54, 08-110 Siedlce, Poland</p>
P-14.	<p><b>Structure and energetic in dissociative electron attachment to the FEBID precursor molecule HFeCo<sub>3</sub>(CO)<sub>12</sub></b>  <u>Ragesh Kumar T P</u>  Science Inst. and Dept. of Chemistry, University of Iceland, Dunhaga 3, 107 Reykjavik, Iceland</p>
P-15.	<p><b>Dissociative electron attachment to HFeCo<sub>3</sub>(CO)<sub>12</sub></b>  <u>Ragesh Kumar T P</u>  Science Inst. and Dept. of Chemistry, University of Iceland, Dunhaga 3, 107 Reykjavik, Iceland</p>
P-16.	<p><b>Electronic state spectroscopy of W(CO)<sub>6</sub> by high-resolution VUV photoabsorption</b>  <u>P. Limao-Vieira</u>  Laboratório de Colisões Atómicas e Moleculares, CEFITEC, Departamento de Física, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal</p>
P-17.	<p><b>OD hits 2D: Size-dependent propagation of Au-clusters on single- and multilayer Carbon Nanomembranes (CNMs)</b>  <u>Paul Penner</u>  Physics of Supramolecular Systems and Surfaces, Bielefeld University, 33615 Bielefeld, Germany</p>
P-18.	<p><b>Synthesis and Thermal Behavior Analysis of Volatile Metal Guanidinate Precursors</b>  <u>Elaheh Pousaneh</u>  Department of Chemistry, TU Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Department of Inorganic Chemistry, Germany</p>
P-19.	<p><b>Synthesis, Characterization and Application of Novel Ruthenium Precursors for MOCVD by a Single Source Approach</b>  <u>Andrea Preuß</u>  Technische Universität Chemnitz, Institute of Chemistry, Inorganic Chemistry, 09107 Chemnitz, Germany</p>

P-20.	<p><b>Electrical transport improvements by post-growth annealing process of cobalt-carbon deposits grown by focused-electron-beam-induced deposition</b></p> <p><u>M. V. Puydinger dos Santos</u></p> <p>EMPA, Swiss Federal Laboratories for Material Science and Technology, Switzerland</p>
P-21.	<p><b>Novel insights into the water-assisted purification of FEBID deposits produced from MeCpPtMe<sub>3</sub></b></p> <p><u>Markus Rohdenburg</u></p> <p>University of Bremen, Institute for Applied and Physical Chemistry, Leobener Straße/NW 2, D-28334 Bremen, Germany,</p>
P-22.	<p><b>Electron-Induced Formation of Cu Nanoparticles from Sequentially Deposited Copper(II)oxalate</b></p> <p><u>K. Rückriem</u></p> <p>Institute of Applied and Physical Chemistry, University of Bremen, D-28334 Bremen, Germany</p>
P-23.	<p><b>Design of atmospheric pressure electron gun with keV energies</b></p> <p><u>Matúš Sámel</u></p> <p>Faculty of mathematics, physics and informatics, Comenius University in Bratislava, Mlynská dolina F2, 842 48 Bratislava, Slovakia</p>
P-24.	<p><b>Surface Modification of Melinex® Films by Electron/Ion Beam Irradiation and XeF<sub>2</sub> Assisted Etching in FIB/SEM Platforms</b></p> <p><u>Meltem Sezen</u></p> <p>Sabancı University Nanotechnology Research and Application Center (SUNUM), Orhanli-Tuzla, 34956, Istanbul, Turkey</p>
P-25.	<p><b>Ab initio studies of the fragmentation of (PMe<sub>3</sub>)Ag(PMe<sub>3</sub>)</b></p> <p><u>Jelena Tamuliene</u></p> <p>Institute of Theoretical Physics and Astronomy, Vilnius University, Sauletekio av. 3, Vilnius, Lithuania</p>
P-26.	<p><b>Computational study of dissociative electron attachment to π-allyl ruthenium (II) tricarbonyl bromide</b></p> <p><u>Rachel M Thorman</u></p> <p>Science Institute and Department of Chemistry, University of Iceland, Dunhagi 3,</p>
P-27.	<p><b>Electron collisions with methyl-substituted ethylenes</b></p> <p><u>Mateusz Zawadzki</u></p> <p>Atomic Physics Division, Department of Atomic, Molecular and Optical Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland</p>

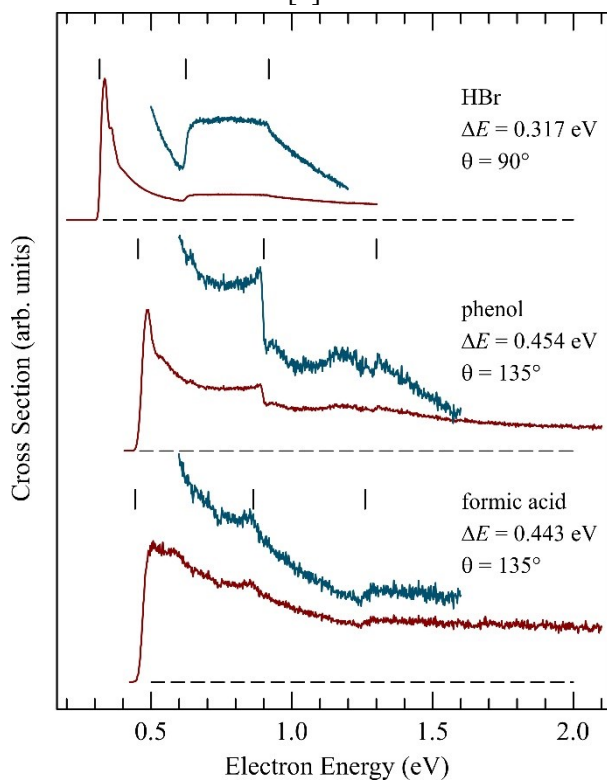
## P-1: On the Puzzling Mechanism of loss of H-Atom in Acidic Compounds: Phenol

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Two theoretical descriptions have been proposed H-loss from acidic compounds. Nonlocal resonance theory is required for example for HBr [1]. The closely related modified effective range R-matrix theory relying on a  $\sigma^*$  resonance was successfully applied to calculate absolute DEA cross sections of formic acid [2] and other molecules.



A mechanism involving electron attachment to a  $\pi^*$  resonance followed by symmetry lowering has been used successfully for acetylene [3,4] and proposed for formic acid [5].

Here we search for evidence for a  $\sigma^*$  resonance in the energy-dependence of the cross section for exciting the O-H stretch vibration of phenol and compare it to the older cases of HBr and formic acid (see figure). We find very similar shapes in all three cases. The cross section enhancement from threshold to 1-1.5 eV is too broad to be explained by direct dipole excitation. On the other hand it differs from a typical  $\pi^*$  resonance band in that the cross section peaks at threshold and has sharp cusp structures at vibrational thresholds.

- [1] M. Čížek, J- Horáček, A.-Ch. Sergenton, D. B. Popović, M. Allan, W. Domcke, T. Leininger and F. X. Gadea, *Phys. Rev. A* **63** (2001) 062710.
- [2] G. A. Gallup, P. D. Burrow and I. I. Fabrikant, *Phys. Rev. A* **79** (2009) 042701.
- [3] S. T. Chourou and A. E. Orel, *Phys. Rev. A* **80**(2009) 034701.
- [4] O. May, J. Fedor, and M. Allan, *Phys. Rev. A* **80**(2009), 012706.
- [5] T. N. Rescigno, C. S. Trevisan, and A. E. Orel, *Phys. Rev. Lett.* **96** (2006) 213201.



## P2: Two-Dimensional Electron Energy Loss Spectra as a Probe of Fast Dynamics in Resonances

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Our initial work on 2D EELS spectra in acrylonitrile [1,2] was extended to benzene, pyridine, diazines, a number of halo-substituted benzenes and pyridines, phenol, p-benzoquinone, nitromethane and  $\text{Fe}(\text{CO})_5$ . The DEA channel is included in the spectra of the compounds where it is open.

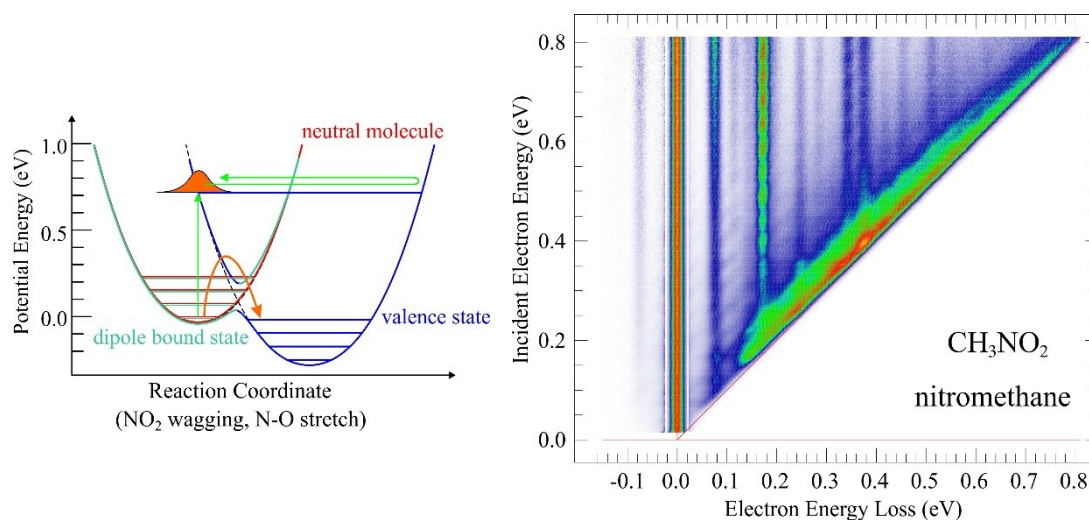


Fig. 1. Nitromethane. Left: Potential energy curves, adopted from reference [3]. Right: 2D spectrum.

The 2D spectra contain rich information about the motion of a nuclear wave packet on a resonant potential surface. In the example of nitromethane (Fig. 1) one sees the boomerang structure due to boomerang motion on the valence diabatic curve (the vertical dotted structure in the 2D spectrum) and a signature of the internal conversion of the dipole-bound state to the 'hot' valence state, decaying by detachment of slow electrons (the diagonal 'threshold ridge').

[1] K. Regeta and M. Allan, *Phys. Rev. Lett.* **110** (2013) 203201.

[2] K. Regeta and M. Allan, *J. Chem. Phys.* **142** (2015) 184307.

[3] T. Sommerfeld, *Phys. Chem. Chem. Phys.* **4** (2002) 2511.

### P-3: Electrons and Ionic Liquids

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Electron Energy Loss Spectra of four representative ILs were recorded in the energy range of electronic excitations and compared to density functional theory multireference configuration interaction (DFT/MRCI) calculations [1], with good agreement (Fig. 1). The spectra up to about 8 eV are dominated by  $\pi$ - $\pi^*$  transitions of the aromatic cations. The lowest bands were identified as triplet states. The spectral region 2-8 eV was empty in the case of a cation without  $\pi$  and  $\pi^*$  orbitals.

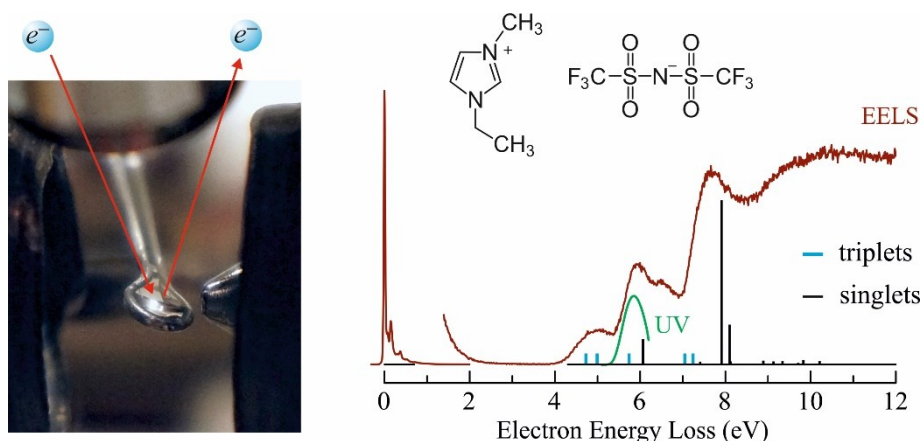


Fig. 1. Left: Photo of the ionic liquid drop in the EEL instrument. Right: A representative EEL spectrum, compared to results of the DFT/MRCI calculation (vertical bars).

The EEL spectrum of a saturated solution of methylene green (MG) dye in an IL band showed the methylene green EEL band at 2 eV, indicating that ILs may be used as a host to study electron collisions with nonvolatile compounds. The MG band was missing in one of the ILs, indicating sensitivity of the method to surface structure. The methylene green EEL band was locally bleached after several hours of measurement, indicating an efficient electron-induced transformation.

[1] K. Regeta C. Bannwarth, S. Grimme and M. Allan, *Phys. Chem. Chem. Phys.* **17** (2015) 15771.

## P-4: FIB/SEM electron tomography and 3D reconstruction of solid oxide fuel cell porous anode

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A Solid Oxide Fuel Cell (SOFC) is an electrochemical device that can convert chemical energy of fuel directly into electricity. A single SOFC consists of two porous electrodes, anode and cathode, separated by an ion conducting solid electrolyte. The complexity of porous structure can be quantitatively described by tortuosity. The tortuosity of an electrode can be defined as a ratio of the real diffusion path length and the electrode thickness. Carman who studied a flow through a bed of sand introduced the concept of tortuosity to porous media study. In his study he assumed that a porous bed of thickness  $L_s$  can be regarded as a bundle of sinuous capillary tubes with a uniform cross section and length  $L_e$  (see Fig. 1a). In this simplified system tortuosity is defined as the ratio of the length of the real diffusion path,  $L_e$ , to the patch in the straight channel case,  $L_s$ . However, in case of a SOFC electrode it is not clear to what extent the idea of Carman's tortuosity can be applied and how to define  $L_e$  in the SOFC electrode where the fuel paths might be extremely complicated and gas communication paths can create many branches, separate and rejoin as it is shown in Fig. 1b. Such a complex structure makes it impossible to clearly define a diffusion path length and consequently the value of the tortuosity. Therefore to precisely describe porous structure authors employ tortuosity factor. Tortuosity and tortuosity factor are two different concepts. Tortuosity factor is derived from the reduction of diffusion in porous structure not from geometrical properties. In the presented study tortuosity factor is quantified by diffusion based simulation. Due to the obstacles the diffusion coefficient in the porous media is smaller than that obtained in a free space. The degree of reduction is described quantitatively using the tortuosity factor.

In this research, electron tomography has been used to reconstruct a three-dimensional image for porous structures from secondary electron (SE) images in a scanning electron microscope (SEM). The implementation of this technique is used to examine the structure of anode after a long-term operation. To calculate tortuosity, a volume of a porous electrode is visualized and numerical simulations are performed.

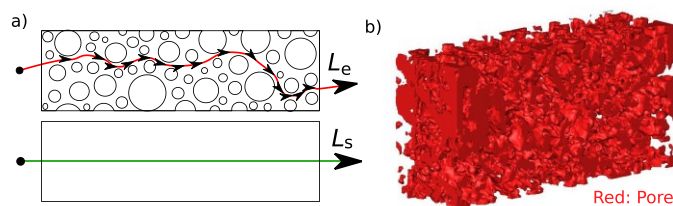


Fig. 1. The concept of tortuosity a) capillary model b) complexity of porous in SOFC anode.

## P-5: Theory in Service of CELINA

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In our contribution we would like to show the progress in the development of our program for calculations of electron scattering by polyatomic molecules. The primary objective of our presentation is to show how our research is oriented to meet the needs of CELINA. In particular it concerns the following issues:

1. New challenges for scattering calculations to meet the needs of CELINA:
  - a short note on relativistic effects and use of pseudopotential for heavy atoms and extension of AO basis sets for f-type and g-type gaussians.
  - calculation of dissociation attachment
2. What we can calculate? Cross sections for gas-phase elastic and vibrationally inelastic electron scattering. Use of resonances in vibrationally inelastic scattering for predictions of precursor decomposition.
3. Choice of precursors to be treated. We are now working on AuClCO and the next precursor should be Pt(PF<sub>3</sub>)<sub>4</sub>. Suggestions for other (preferably small) would be appreciated.
4. Present state of the program development and scattering calculations.

## **P-6: Quantum chemical characterization of dopamine.**

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Inside the brain, dopamine functions as a neurotransmitter and neuromodulator. It plays important roles in executive functions, motor control, motivation, reinforcement and reward, as well as in lower-level functions, including lactation, sexual gratification, and nausea. The disturbances in its secretion, uptake, or storage are associated with a multitude of medical conditions, including Parkinson's disease, attention deficit hyperactivity disorder, schizophrenia, and addictions. The neurotransmitters are the key points in translating the physical information (the change of electrochemical potential of nervous cells – flow of electrons) into a chemical one (release of molecules), with the biological consequences.

Therefore, they became an object of our studies.

Here, we present the quantum chemical characteristic of an isolated molecules of dopamine. We discuss the relative stability of its tautomeric forms, as well as its ionization potentials and electron affinities. Our results suggest that the electric impulse (an excess electron) may act as a trigger – the quasi-stable anionic states of a dipole-bound character induce the change of a direction of catechololn –OH groups, altering the relative shares of tautomers in thermodynamic equilibrium.

## P-7: Electron induced fluorescence of acetylene

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The collisions of slow electrons with molecules play an important role in many phenomena, such as atmospheric processes induced by radiation from space, low temperature plasma, secondary and back scattered electrons in radiation chemistry and FEBID technologies, etc. The electron induced fluorescence spectroscopy is one of the methods that can be used to study interactions of low energy electrons with molecules and provide new data on the excitation, dissociation and ionization processes in atoms and molecules. The acetylene, the smallest hydrocarbon molecule with triple bond, is often used in plasma polymerization, for deposition of diamond like carbon layers and it is abundant in space [1, 2]. This molecule was also used as a ligand in metalorganic compounds [3]. From the spectroscopic point of view, acetylene is among the most studied molecules, however, the excitation-emission cross section data are incomplete and sometimes contradictory.

Electron impact excitation of acetylene ( $C_2H_2$ ) was studied using a crossed beam apparatus described in detail in [4]. The apparatus utilizes crossed beams of molecules and monochromatic electrons with typical energy resolution of 300-400 meV. The system of mirrors and lenses guides the photons emitted during deexcitation to the entrance slit of the Czerny-Turner optical monochromator with thermoelectrically cooled photo multiplier tube working in photon counting regime.

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

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[1] S. Boyé et al., *J. Chem. Phys.* **116** (2002) 8843.

[2] A. Tanabashi et al., *Astrophys. Suppl. Series* **169** (2007) 472.

[3] H. G. Alt und H. E. Engelhardt, *Z. Naturforsch.* **42b** (1987) 711.

[4] M. Danko et al., *J. Phys. B: At. Mol. Opt. Phys.* **46** (2013) 045203.

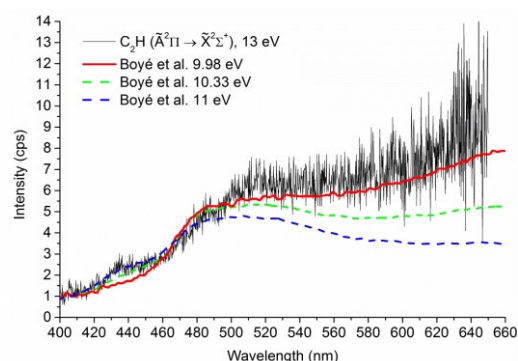


Fig. 1. Continuum radiation of  $C_2H_2$ .

## P-8: Electron-Driven Proton Transfer in Hydrogen-Bonded Systems

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Intermolecular proton transfer in hydrogen bonded complexes has been studied computationally and experimentally using anion photoelectron spectroscopy (PES) technique. We will present results for model hydrogen bonded systems and for complexes involving nucleic acid bases. Anion photoelectron spectroscopy and electron energy-loss spectroscopy (EELS) probe different regions of the anionic potential energy surface. These complementary techniques provided information about anionic states of acetoacetic acid (AA). Electronic structure calculations facilitated the identification of the most stable tautomers and conformers for both neutral and anionic AA, and determined their relative stabilities and excess electron binding energies. The valence anion displays a distinct minimum which results from proton transfer from the carboxylic to the keto group, thus we name it an ol structure. The minimum is characterized by a short intramolecular hydrogen bond, a significant electron vertical detachment energy of 2.38 eV, but a modest adiabatic electron affinity of 0.33 eV. The valence anion was identified in the anion PES experiments and the measured electron vertical detachment energy of 2.30 eV is in good agreement with our computational prediction. The results of EELS experiments do not provide evidence for an ultrarapid proton transfer in the lowest  $\pi^*$  resonance of  $AA^-$ , which would be capable of competing with electron autodetachment. This observation is consistent with our computational results indicating that major gas phase conformers and tautomers of neutral AA do not support the intramolecular hydrogen bond that would facilitate ultrarapid proton transfer and formation of the ol valence anion. This is confirmed by our vibrational EELS spectrum.

[1] Z.G. Keolopile, M. Gutowski, A. Buonaugurio, E. Collins, X. Zhang, J. Erb, T. Lectka, K.H. Bowen, M. Allan, *J. Am. Chem. Soc.* **137** (2015) 14329.

## P-9: Magnetic properties of electrodeposited Pt-CoPt nanowire arrays

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The basic problem limiting the practical application of nanomaterials are the relatively high costs of their manufacture. Therefore, efforts focusing on the development of new, relatively easy to implement, and above all, inexpensive methods for the preparation of nanomaterials are made. Among numerous methods, vapor deposition methods (chemical and physical), chemical and electrochemical methods are of particular interest. The latter in particular as it allows to obtain materials with a strictly controlled composition and architecture, is cost-effective and operates at temperatures near room temperature [1].

Although the electrochemical deposition of multilayered nanomaterials has already been described elsewhere, we focus on thorough studies of electrochemical synthesis of multilayered nanowires consisting of magnetic - CoPt alloy, and nonmagnetic - Pt segments. Detailed research on the influence of their thickness on the magnetic properties of multilayered nanowire arrays was conducted. Furthermore, we determined the mechanism of magnetization reversal in Co-Pt multilayered nanowire arrays and its dependence on the magnetic-segment thickness [2].

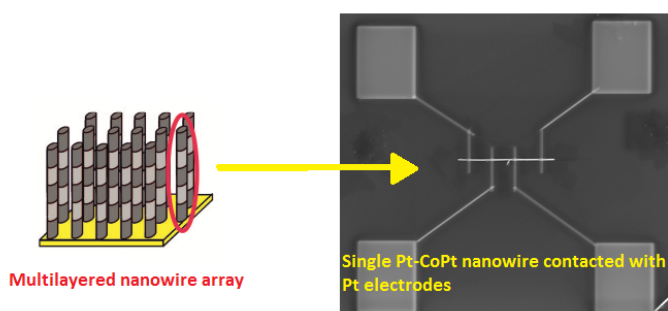


Fig. 1. Schematic representation of nanowire array together with SEM image of single multilayered nanowire contacted with platinum electrodes (Pt contacts obtained via Focused – Electron – Beam – Induced – Deposition (FEBID) from MeCpPtMe<sub>3</sub> precursor).

Acknowledgments: The research was partially carried out thanks to the financial support of the Ministry of Science and Higher Education Iuventus Plus Program (project no. IP2014 0152 73).

[1] K.E. Hnida, S. Bäßler, L. Akinsinde, J. Gooth, K. Nielsch, R.P. Socha, A. Łaszcz, A. Czerwinski, G.D. Sulka, *Nanotechnology* **26** (2015) 285701.

[2] K.E. Hnida, A. Żywczak, M. Gajewska, M. Marciszko, G.D. Sulka and M. Przybylski, *Electrochim. Acta* **205** (2016) 29.



## P-10: Low-energy electron interactions with chromium hexacarbonyl

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The application of Focused Electron Beam Induced Deposition (FEBID) allows the development of functional nanoscale structures on surfaces. One problem in FEBID is the purity-level of the deposit, which influences the function as well as the resistivity of the created deposit [1,2]. Impurities can result due to incomplete decomposition, i.e., the presence of precursor organic ligands. Therefore the understanding of different reactions occurring during FEBID is crucial so that the amount of impurities can be minimized, aiming for a pure deposit. In particular, it is assumed that both the purity and the spatial resolution of the deposit depend on interactions of the deposit with secondary low-energy electrons [3].

Chromium containing compounds are used in FEBID as precursor molecules due to the high purity of the deposit-structure [1,4,5]. In this work, interaction of low energy electrons with organometallic chromium hexacarbonyl ( $\text{Cr}(\text{CO})_6$ ) in the gas phase was investigated for electron energies between  $\sim 0\text{--}70$  eV. All measurements were carried out using a double focusing two sector field mass spectrometer in reversed Nier-Johnson geometry. In both cases, cation as well as anion formation, a strong sequential loss of CO-ligands was found. Additionally, the bare chromium ion ( $\text{Cr}^+/\text{Cr}(\text{CO})_6$  and  $\text{Cr}^-/\text{Cr}(\text{CO})_6$ ) was observed.

Acknowledgements: The present work was partially supported by the Austrian Funding Agency, FWF (I1015) and the COST Action CM1301 (CELINA).

- [1] A. Botman, J.J.L. Mulders, C.W. Hagen, *Nanotechnology* **20** (2009) 17.
- [2] M. Huth, F. Porrati, C. Schwalb, M. Winhold, R. Sachser, M. Dukic, J. Adams and Georg Fantner, *Beilstein J. Nanotechnol.* **3** (2012) 597.
- [3] R. M. Thorman, R. Kumar T. P., D. H. Fairbrother, O. Ingólfsson, *Beilstein J. Nanotechnol.* **6** (2015) 1904.
- [4] N.A. Kislov, I.I. Khodos, E.D. Ivanov, J. Barthel, *Scanning* **18** (1996) 114.
- [5] R.R. Kunz, T.M. Mayer, *J. Vac. Sci. Technol. B.* **6** (1988) 1557.

## **P-11: Radiation reduced CNM formation from halogenated biphenylthiols**

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The ability to produce, control and investigate homogenous 2D materials as e.g. graphene gives access to thoroughgoing physical and chemical properties for new technological applications and devices. Carbon Nano Membranes (CNM), comparable to graphene, are mechanical stable quasi 2D systems which are formed by the electron radiation induced cross linking of molecules in specific self-assembled monolayers (SAM) grown on a Au(111) substrate. This allows the tailoring of the CNMs structural and functional properties by the selection and composition of appropriate precursors for the SAM formation like for instance phenylthiols or naphthalenes [1,2].

Here we present the study of halogenated biphenylthiols which show in contrast to normal biphenylthiols a lowered stability on the influence of heat, light or electric fields. This at the first glance disadvantage is used for a favoured reduction of the needed radiation intensity for the conversion of the SAM into a stable CNM.

[1] P. Angelova et al., *ACS Nano* **7** (2013) 6489.

[2] A. Turchanin et al., A. Götzhäuser, *Adv. Mater.* **21** (2009)1233.

## P-12: Gas sensing properties of CuO/Fe<sub>2</sub>O<sub>3</sub> heterostructures

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The motivation of this work is to study gas sensing properties of Fe<sub>2</sub>O<sub>3</sub>/CuO heterostructures towards recognition of acetone. Numerous studies in recent years related to acetone detection in the exhaled human breath appeared have due to the fact that C<sub>3</sub>H<sub>6</sub>O is considered as a biomarker of diabetes [1]. The results of our work shall expand the knowledge on synthesis route and optimum structure of nanomaterials based on Fe<sub>2</sub>O<sub>3</sub>/CuO which is crucial for improving the acetone sensing behavior. Several techniques were applied to study the sputtered heterostructures: the morphology of the samples was tested by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Fig.1a). Chemical composition was tested by means of electron microprobe X-ray fluorescence (TEM-EDX) and X-ray photoelectron spectroscopy (XPS). The gas sensing properties of the examined Fe<sub>2</sub>O<sub>3</sub>/CuO heterostructures towards low concentrations of acetone in the exhaled breath are compared in Fig. 1b.

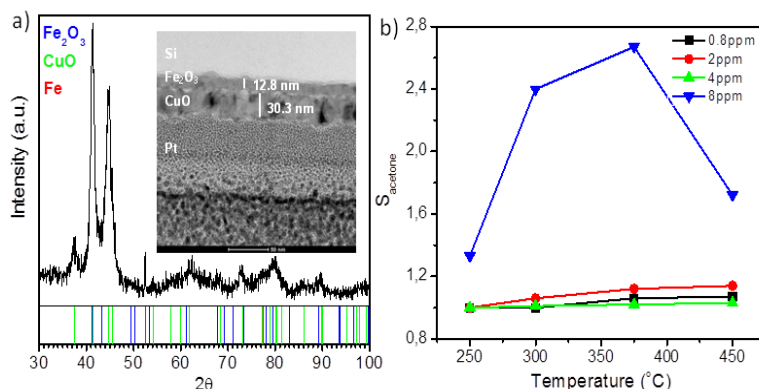


Fig. 1 a) XRD pattern with a TEM cross-section image and b) sensor response  $S$  upon interaction with acetone at various temperatures of Fe<sub>2</sub>O<sub>3</sub>/CuO heterostructure deposited by rf/dc magnetron sputtering.

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[1] M. Ye, P.-J. Chien, K. Toma, T. Arakawa, K. Mitshubayashi, *Biosens. Bioelectron.* **73** (2015) 208.

## P-13: Reactions driven in chloro(dimethyl sulfide)gold(I) by low energy electrons

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Interaction of gold with various ligands is one of the most interesting interfacial chemistry for wide range of research fields such as surface and material science with applications in technology, drug delivery and medical therapies. In particular the bonding between gold and sulfur remains the most common interaction for the formation of nanostructures by adsorption of organic molecules onto a solid surface known as self-assembled monolayers SAM [1]. The Au-thiol is often used to immobilize a DNA terminus on a substrate [2,3]. The DNA can be anchored to the metal surface via a standard modification of the phosphate moiety to form P=S. Gold halides are also of great interest since they are known to exhibit a rich chemistry [4]. For instance gold(I) chloride, AuCl, has some semiconductor properties such as luminescence of exciton at 480 nm (2.57 eV) as it has been reported in [5,6].

Here we discuss the fragmentation of chloro(dimethyl sulfide)gold(I) caused by low energy electrons. The most dominant reaction channel leads to the formation of chlorine anion due to a simple Au-Cl bond cleavages. Our data show that the thiolated ligand is less sensible towards the interaction with low energy electrons. Indeed the yield of the fragments generated from the dimethylsulfur site are around one order of magnitude lower than the yield of chlorine anion.

Acknowledgments: This work has been supported by the Polish Ministry of Science and Higher Education (project 277/S/11).

[1] R.G. Nuzzo, D.L. Allara, *J. Am. Chem.Soc.* **105** (1983) 4481.

[2] P.A. Alivisatos, et al. *Nature* **382** (1996) 609.

[3] H. Abdoul-Carime, L. Sanche, *Surf. Sci.* **451** (2000) 102.

[4] R.J. Puddephatt, in *Chemistry of Gold*, Edit. R.J.H; Clark, Elsevier New York (1978).

[5] T.N. Silukova, P.A. Babin, S.F. Voropaev, V.G. Plekhanov, *Opt. Spectrosc (USSR)* **46** (1979) 218.

[6] F. Zehani, M. Sebais, H. Zaïoune, *J. Mod. Phys.* **3** (2012) 534.

## **P-14: Structure and energetic in dissociative electron attachment to the FEBID precursor molecule $\text{HFeCo}_3(\text{CO})_{12}$**

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$\text{HFeCo}_3(\text{CO})_{12}$  is a organometallic precursor molecule that has been used in chemical vapour deposition to deposit FeCo thin films [1]. Recently this precursor molecule was tested in FEBID to fabricate FeCo magnetic alloy nanostructures [2], making it the first heteronuclear precursor molecule used in FEBID to fabricate bi-metallic nanostructures. In light of the role of low energy secondary electrons in the deposition process (see e.g., ref [3] and references therein) we have conducted a study on dissociative electron attachment (DEA) to this molecule in the energy range from about 0 to above 20 eV.

Furthermore, to aid the interpretation of the DEA data we employed BP86/def2-TZVP level of theory to optimise the structure of  $\text{HFeCo}_3(\text{CO})_{12}$  and its molecular anion. The calculated optimised structure of the neutral molecule agrees well with the structure determined from single crystal XRD [2,4]. From the optimised structure of the molecular anion and the HOMO and SOMO analysis, we observed that during the attachment of electron the Fe-Co bonds are elongated and a bridging CO bond is formed between Fe and one Co with high spin density at the apex Fe. These calculations agree well with our experimental observations, in which  $\text{Fe}(\text{CO})_4^-$  is found to be the second most abundant fragment. Based on the single point energy calculated at the BP86/def2-TZVP and PBE0/ma-def2-TZVP levels of theory we also determine the thermochemical threshold for sequential loss of CO and the loss of the epical Fe group (as  $\text{Fe}(\text{CO})_3^-$  and  $\text{Fe}(\text{CO})_4^-$ ). We compare the calculated threshold with experimentally determined appearance energy and find that the calculated thresholds at the BP86/def2-TZVP level of theory are significantly higher than the determined appearance energies, while the thresholds calculated at the PBE0/ma-def2-TZVP level of theory are concordant with the observed appearance energy.

Acknowledgments: This work was supported by Icelandic Centre for Research (RANNIS). R. K. T. P acknowledges a PhD grant from the University of Iceland Research Fund and an STSM support from the COST Action CM1301 (CELINA).

[1] C. L. Czekaj-Korn and G. L. Geoffroy, *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*. 157-164 (1988).

[2] F. Porrati, M. Pohlit, J. Müller, S. Barth, F. Biegger, C. Gspan, H. Plank and M. Huth, *Nanotechnology* **26** (2015) 475701.

[3] R. M. Thorman, R. Kumar T. P., D. H. Fairbrother, O. Ingólfsson, *Beilstein J. Natotechnol.* **6** (2015) 1904.

[4] Ragesh Kumar T P, Sven Barth, Ragnar Bjornsson and Oddur Ingólfsson, *European Physical Journal D*, Submitted.

## P-15: Dissociative electron attachment to $\text{HFeCo}_3(\text{CO})_{12}$

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In the current contribution we report dissociative electron attachment (DEA) measurements of the bimetal precursor molecule  $\text{HFeCo}_3(\text{CO})_{12}$  in the energy range 0 to 27 eV.  $\text{HFeCo}_3(\text{CO})_{12}$  has been used in chemical vapor deposition to make FeCo thin films [1], very recently this precursor molecule was used in focused electron beam induced deposition (FEBID) to make FeCo nanostructures [2]. FEBID is working on the basis of electron beam induced dissociation and during the FEBID process large number of secondary electrons (SE, energy < 50 eV) are produced from the substrate and the growing deposit. The interaction of these SEs with precursor molecules plays a significant role in determining the ultimate resolution and the purity of structures fabricated with FEBID (see e.g., ref [3] and references therein). Motivated by this notation the current study is intended to contribute to the understanding of low energy SE interaction with  $\text{HFeCo}_3(\text{CO})_{12}$ .

In the energy range from about 0 to 20 eV, we observed three main DEA patterns. Negative ions observed in the first are  $\text{Fe}(\text{CO})_4^-$ ,  $\text{Fe}(\text{CO})_3^-$  and  $\text{Fe}(\text{CO})_2^-$ , the second constitutes sequential CO loss extending from about 0 eV for single CO loss to about 20 eV for the formation of  $[\text{M} - 12\text{CO}]^-$ , hence to about 12 eV above the ionization potential of this molecule. Preliminary we attributed this observation to a quasi continuum electron attachment leading to core excited resonances partly associated with multiple electronic excitation. In order to support this notation and better understand the nature of this attachment process we have calculated the density of states for this compound and related compounds without direct metal to metal bonds.

The third pattern observed is that of the formation of  $[\text{M} - \text{Co}(\text{CO})_n]^-$ , where n varies from 4 to 10. In addition, we also observe the parent negative ion  $\text{M}^-$ . The dominant negative ion formed in DEA is  $[\text{M} - 2\text{CO}]^-$ .

Acknowledgments: This work was supported by Icelandic Centre for Research (RANNIS). R. K. T. P acknowledges a PhD grant from the University of Iceland Research fund and an STSM support from the COST Action CM1301 (CELINA).

[1] C. L. Czekaj-Korn, G. L. Geoffroy, *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*. 157-164 (1988).

[2] F. Porrati, M. Pohlit, J. Müller, S. Barth, F. Biegger, C. Gspan, H. Plank, M. Huth, *Nanotechnology* **26** (2015) 475701.

[3] R. M. Thorman, R. Kumar T. P., D. H. Fairbrother, O. Ingólfsson, *Beilstein J. Natotechnol.* **6** (2015) 1904.

## P-16: Electronic state spectroscopy of W(CO)<sub>6</sub> by high-resolution VUV photoabsorption

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The role of metal carbonyl complexes has been fully acknowledged in recent years in the field of plasma technology for metallic layers preparation [1] as well as in nanotechnology to deliver metallic structures [2, 3]. Tungsten hexacarbonyl is one of the most important because of its chemical properties well-attuned to prepare tungsten layers and tungsten interconnection in Electron Beam Induced Deposition (EBID) and Ion Beam Induced Deposition (IBID) techniques [4–7]. As so, in these high-energy (tens of keV) electron- and ion-driven processes, low-energy secondary electrons (< 100 eV) are produced by the interaction of the primary beam with the surface and surface deposits, which can trigger efficient dissociative ionisation and electron attachment reactions to deposited organometallic molecules on the surface of a solid substrate. Moreover, electron interactions with these molecules are also responsible for other inelastic processes (e.g. electronic excitation) and so detailed information of the electronic states of these molecules is needed. Yet, we note that comprehensive descriptions of the low-lying electronic and ionic states are limited to old publications in very limited wavelength regions [8, 9] at low-resolutions. Therefore, we have performed comprehensive high-resolution VUV photoabsorption measurements (110-350 nm) and we are combining these with full support of theoretical calculations for the electronic states.

- [1] K.K. Lai, H.H. Lamb, *Thin Solid Films* **370** (2000) 114.
- [2] C.W. Hagen, W.F. van Dorp, P.A. Crozier, P. Kruit, *Surf. Sci.* **602** (2008) 3212.
- [3] K.E. Lewis, D.M. Golden, G.P. Smith, *J. Am. Chem. Soc.* **106** (1984) 3905.
- [4] I. J. Luxmore, I.M. Ross, A.G. Cullis, P.W. Fry, J. Orr, P.D. Buckle, *Thin Solid Films* **515** (2007) 6791.
- [5] M. Song, K. Furuya, *Sci. Technol. Adv. Mater.* **9** (2008) 023002.
- [6] F. Porriati, R. Sachser, M. Huth, *Nanotechnology* **20** (2009) 195301.
- [7] I. Sychugov, Y. Nakayama, K. Mitsuishi, *J. Phys. Chem. C* **113** (2009) 21516.
- [8] N.A. Beach, H.B. Gray, *J. Am. Chem. Soc.* **90** (1968) 5713.
- [9] A. Iverson, B.R. Russels, *Chem. Phys. Lett.* **6** (1970) 307.

## **P-17: 0D hits 2D: Size-dependent propagation of Au-clusters on single- and multilayer Carbon Nanomembranes (CNMs)**

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CNM is a two-dimensional amorphous carbon material with a thickness of a single molecule (~1 nm) and tunable surface chemistry. The irradiation of aromatic self-assembled monolayer with electrons leads to the cleavage of C-H bonds and the lateral crosslinking of the carbon atoms. The result is a soft but mechanical stable two-dimensional carbon network which gives rise to many possible applications like gas filtration and TEM sample support for nanoparticles or biological specimens. Au-Clusters owing quantum size effects, which depend on the number of atoms, and therefore offer many fascinating properties used in catalysis, optics and biological labeling. Cluster beam deposition in combination with a lateral time-of-flight mass selector offers the possibility to control the size of clusters und therefor its unique properties. Au-clusters were deposited on single- and multilayers of CNMs made from various precursors with different functionality to introduce nanoscale defects and investigate surface-cluster interaction. The investigation was done with aberration-corrected scanning transmission electron microscopy in high angle annular dark field mode. Due to its small thickness and light element composition CNMs are ideal supports for the investigation of clusters. An energy of  $34 \pm 6$  eV/atom, corresponding  $\sim 17$  MJ/kg (compared to a single layer graphene 1.2 and Kevlar 0.5 MJ/kg), is necessary for Au-clusters to perforate one layer of CNM. First measurements have implied that the stopping power of CNMs obeys a universal behavior, where the implantation depth depends on the momentum of the clusters.



## P-18: Synthesis and Thermal Behavior Analysis of Volatile Metal Guanidinate Precursors

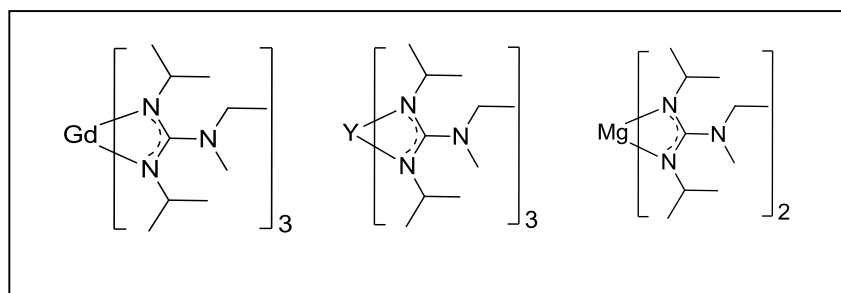
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Metal oxides (e.g.  $Gd_2O_3$ ,  $Y_2O_3$  and  $MgO$ ) have received special interest as high- $\kappa$  materials for metal-oxide semiconductor field-effect transistors. Metal guanidinate precursors are promising complexes for being used in chemical vapor deposition (CVD) or atomic layer deposition (ALD) studies, since it is expected that they (i) increase the reactivity of the complexes towards water, (ii) increase the surface coverage, (iii) show high growth rates, (iv) are capable to produce metal nitrides, (v) and produce thin films with minimal carbon impurity. In addition, these ligands are expected to increase the volatility as well as stability of the respective dimeric or trimetric metal complexes and making them suitable for CVD and ALD deposition processes[1,2,3]. Within this study, we have synthesized different metal guanidinate precursors by the reaction of lithium guanidinate with different metal chlorides. Thermal gravimetric (TG) studies were carried out under oxygen and nitrogen flow to gain information about the thermal behavior of the precursors under different conditions.

Here we report the synthesis of homoleptic guanidinate complexes of gadolinium, yttrium and magnesium. Gadolinium and yttrium compounds are volatile solids, while the respective magnesium complex is a liquid and distills at low temperature.



- [1] A. P. Milanov, T. Toader, H. Parala., D. Barreca, A. Gasparotto, C. Bock, H. W. Becker, D. K. Ngwashi, R. Cross, S. Paul, U. Kunze, R. Fischer, A. Devi, *Chem. Mater.* **21** (2009) 5443.  
[2] A. P. Milanov, K. Xu, S. Cwik, H. Parala, T. de los Arcos, H -W. Becker, D. Rogalla, R. Cross, S. Paul, A. Devi, *Dalton Trans.* **41** (2012) 13936.  
[3] A. Kurek, P. G. Gordon, S. Karle, A. Devi, S. T. Barry, *Aust. J. Chem.* **67** (2014) 989.

## P-19: Synthesis, Characterization and Application of Novel Ruthenium Precursors for MOCVD by a Single Source Approach

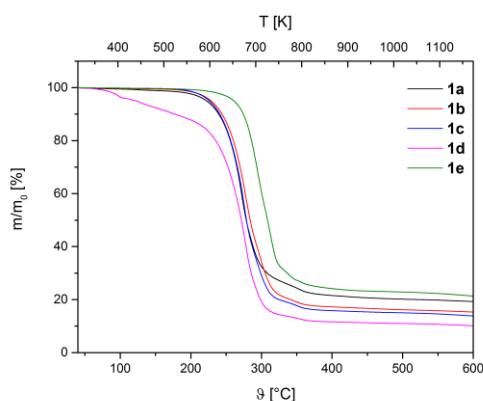
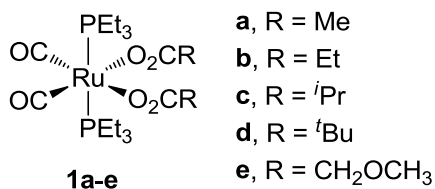
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Thin ruthenium layers are promising candidates for many applications in semiconductor industry [1]. However, their use as diffusion barrier for copper interconnects in integrated circuits is limited, due to grain boundaries of a polycrystalline structure allowing copper diffusion at unacceptable low temperatures [2]. Amorphous ruthenium-based films, *e.g.* obtained by incorporation of phosphorus, have been shown to provide better copper diffusion barrier properties than pure polycrystalline ruthenium deposits [3].

We herein present the synthesis and characterization of ruthenium precursors of general type  $\text{Ru}(\text{CO})_2(\text{PEt}_3)_2(\text{O}_2\text{CR})_2$  ( $\text{R} = \text{Me}, \text{Et}, i\text{Pr}, t\text{Bu}, \text{CH}_2\text{OCH}_3$ ) and their use as single-source CVD precursors for the preparation of thin and conformal phosphorus-doped ruthenium layers. Variation of the phosphine and carboxylate ligands allowed influencing the thermal behavior and vapor pressure of the respective precursor [4].



- [1] A. Tuchscherer, C. Georgi, N. Roth, D. Schaarschmidt, T. Ruffer, T. Wächtler, S. E. Schulz, S. Oswald, T. Gessner, H. Lang, *Eur. J. Inorg. Chem.* (2012) 4867.
- [2] L. B. Henderson, J. G. Ekerdt, *Thin Solid Films* **517** (2009) 1645.
- [3] J.-H. Shin, H.-W. Kim, K. Agapiou, *et al.*, *J. Vac. Sci. Technol. A* **26** (2008) 974.
- [4] J. Jeschke, S. Möckel, M. Korb, T. Ruffer, K. Assim, M. Melzer, G. Herwig, C. Georgi, S. E. Schulz, H. Lang, *J. Mater. Chem. C* (2016) 2319.

## P-20: Electrical transport improvements by post-growth annealing process of cobalt-carbon deposits grown by focused-electron-beam-induced deposition

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Co<sub>2</sub>(CO)<sub>8</sub> FEBID was performed with 15 keV electrons and 1.5 nA beam current on (100 nm) SiO<sub>2</sub>/Si substrates pre-structured with Pt-electrodes in a tungsten cathode SEM (electronic flux ~ 3 × 10<sup>18</sup> s<sup>-1</sup>·cm<sup>-1</sup>). The non-thermal dissociation of the precursor adsorbates resulted in co-deposition of carbon and oxygen from the carbonyl ligands and a granular structure consisting of Co nanocrystals embedded in an amorphous C-O matrix (Co:C:O = 67:14:19 at.%). In contrast, Co<sub>2</sub>(CO)<sub>8</sub> FEBID using high-brightness field emission guns resulted in pure (up to 96 at.%) cobalt material [1]. Post-growth annealing was carried out at 100°C, 200°C and 300°C during 10 minutes below 3 × 10<sup>-5</sup> mbar and the four-probe resistance of the deposits measured at room temperature. The resistivity values (Fig. 1) decrease from 26 mΩ·cm (as-deposited) down to 26 μΩ·cm (300°C), which is only twice the value of pure Co films reported for Physical Vapor Deposition with similar dimensions [2]. Interestingly, the resistivity is lower by a factor of two than reported for the purest Co (96 at.%) ever defined by FEBID [1]. Energy-dispersive X-ray spectroscopy (EDX) shows that it is mainly oxygen that leaves the deposit while Raman spectroscopy indicates a partial thermally-induced conversion of amorphous carbon matrix into graphite nanocrystals contributing to electrical conductivity.

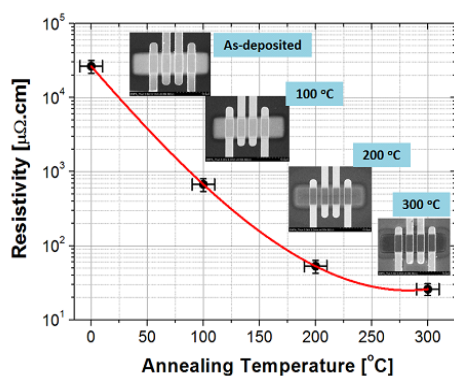


Fig. 1. Resistivity in function of annealing temperature of Co<sub>2</sub>(CO)<sub>8</sub> FEBID.

[1] A. Fernández-Pacheco, J. M. De Teresa, R. Córdoba, M. R. Ibarra, *J. Phys. D: Appl. Phys.* **42** (2009).

[2] J. W. C. DeVries, *Thin Solid Films* **167** (1988) 2532.

## P-21: Novel insights into the water-assisted purification of FEBID deposits produced from MeCpPtMe<sub>3</sub>

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The widely applied FEBID precursor trimethyl(methylcyclopentadienyl)-platinum(IV) (MeCpPtMe<sub>3</sub>) is renowned as a ‘notoriously bad’ precursor typically yielding deposits with a Pt content of only about 20% [1, 2]. Fundamental studies have identified the reason for the low Pt content of FEBID deposits produced from MeCpPtMe<sub>3</sub>. It was found that DEA predominantly leads to the loss of only one CH<sub>3</sub> group from the precursor [3]. This exactly matches the typical deposit composition of Pt:C = 1:8 obtained under UHV conditions, i.e., without contributions of residual vapours to deposit formation [2]. The ligand material remaining after loss of the first CH<sub>3</sub> thus becomes embedded in the deposit, a result that underlines, at the same time, the importance of low-energy electron-induced chemistry in FEBID processes.

Surprisingly, it was shown very recently and in contrast to earlier attempts [4] that deposits produced from MeCpPtMe<sub>3</sub> can be efficiently purified by a post-deposition electron beam treatment in the presence of water vapour thus yielding densely packed carbon- and oxygen-free Pt material [5]. The authors suggested that the initial carbon content diffuses to the surface of the deposit and desorbs as small volatile products (CO, CO<sub>2</sub>, CH<sub>x</sub>). Herein, a study applying a combination of electron-stimulated desorption (ESD) experiments and thermal desorption spectrometry (TDS) of electron-induced and water-assisted reactions in thin condensed layers of MeCpPtMe<sub>3</sub> is presented. In addition, deposit composition was monitored by Auger electron spectroscopy (AES). The results give insight into the electron-induced reactions of MeCpPtMe<sub>3</sub> in the presence of water. The lack of precursor hydrolysis in the absence of an electron beam underlines that the purification relies on the synergy between water and electron irradiation.

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

[2] J.D.Wnuk, J.M.Gorham, S.Rosenberg, W.F.van Dorp, T.E.Madey, C.W.Hagen, D.H.Fairbrother, *J.Phys.Chem. C* **113** (2009) 2487.

[3] S. Engmann, M. Stano, Š. Matejčík, O. Ingólfsson, *Phys. Chem. Chem. Phys.* **14** (2012) 14611.

[4] Botman, J.J.L.Mulders, C.W.Hagen, *Nanotechnology* **20** (2009) 372001.

[5] B. Geier, C. Gspan, R. Winkler, R. Schmied, J.D. Fowlkes, H. Fitzek, S. Rauch, J. Rattenberger, P.D. Rack, H. Plank, *J. Phys. Chem. C* **118** (2014) 14009.

## P-22: Electron-Induced Formation of Cu Nanoparticles from Sequentially Deposited Copper(II)oxalate

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Nanoscale materials display particular physical and chemical properties as compared to the bulk of same composition. When grown or deposited on a surface they can thus provide their support with a wide range of useful functions. Although not as prominent as their Au and Ag analogues, nanoparticles (NPs) of the more affordable metal Cu exhibit similarly useful properties [1-4]. A number of applications has consequently been proposed. This includes, among others, the application as antibacterial and antifungal agents, the use of supported Cu NPs as catalysts, as substrate for surface-enhanced Raman scattering (SERS), and potentially a range of further plasmonic applications.

We have recently established a layer-by-layer deposition procedure to produce well-defined surface layers of copper(II)oxalate [5]. On a carboxy-terminated self-assembled monolayers these layers were grown using a step-by-step approach by dipping the surfaces alternately in ethanolic solutions of copper(II)acetate and oxalic acid with intermediate thorough rinsing steps. The deposition was monitored by reflection absorption infrared spectroscopy (RAIRS), a quartz microbalance with dissipation measurement (QCM-D), scanning electron microscopy (SEM), and Helium ion microscopy (HIM). Here, we show that such layers can be efficiently transformed to pure Cu NPs by low-energy electron irradiation at room temperature. This process also offers the perspective of adding capping layers in-situ via an electron-induced deposition process from the gas phase thus addressing the potential problem of Cu oxidation.

[1] X. Zhu, B. Wang, F. Shi, J. Nie, *Langmuir* **28** (2012) 14461.

[2] M.D. Susman, Y. Feldman, A. Vaskevich, I. Rubinstein, *Chem. Mater.* **24** (2012) 2501.

[3] Y. Wei, S. Chen, B.Kowalczyk, S. Huda, T.P. Gray, B.A. Grzybowski, *J. Phys. Chem. C* **114** (2010) 15612.

[4] D.B. Pedersen, S. Wang, *J. Phys. Chem. C* **111** (2007) 17493.

[5] I. Schrader, L. Wittig, K. Richter, H. Vieker, A. Beyer, A. Gölzhäuser, A. Hartwig, P. Swiderek, *Langmuir* **30** (2014) 11945.

## P-23: Design of atmospheric pressure electron gun with keV energies

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Electron guns are devices used to generate electron beams and are used as ion sources in plenty of analytical applications such as mass spectrometry, electron welding, Scanning Electron Microscopy (SEM) and many others. One of the possible application of electron guns with keV electron energy is Focus Electron Beam Induced Deposition (FEBID), which is used for deposition of metallic nanostructures by interaction of high-energetic electrons with organometallic compounds. Recently, electron guns with nanomembrane vacuum-atmosphere interface (window) of 300 nm thickness were developed, which allow transport of keV electrons from vacuum to atmosphere [1 - 3].

We developed similar source of electrons, which can be used to study electron interactions with molecules in vacuum or at atmospheric pressure. This electron gun allows transmission of electrons at considerable lower energies and with higher electron currents as reported in earlier studies [1 - 3]. In contrast to the earlier studies we have used  $\text{Si}_3\text{N}_4$  nanomembrane of 100 nm thickness. The results are shown in Figure 1. We have measured electron current, which penetrated the membrane in vacuum as function of acceleration voltage and for different filament emission currents. The threshold energy for penetration of electrons through the window was below 3 keV. For the filament emission current of 50  $\mu\text{A}$  almost 1  $\mu\text{A}$  electron current penetrated through the membrane.

These first results are very promising and we hope that this electron source will allow us to study electron excitation and ionisation processes at elevated pressure.

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[1] F. Gunzer, A Ulrich, W Baether, *Int. J. Ion. Mob. Spec.* **13** (2010) 9.

[2] P. Cochems, J. Langejuergen, A. Heptner, S. Zimmermann, *Int. J. Ion. Mob. Spec.* **15** (2012) 223.

[3] P. Cochems, M. Runge, S. Zimmermann, *Sens. Act. A206* (2014) 165.

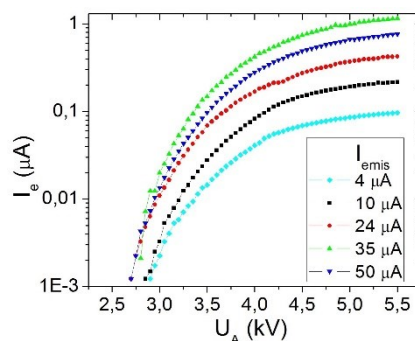


Figure 1: Dependence of electron current from acceleration voltage

## **P-24: Surface Modification of Melinex<sup>®</sup> Films by Electron/Ion Beam Irradiation and XeF<sub>2</sub> Assisted Etching in FIB/SEM Platforms**

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Applications of polymeric material are increasingly spreading over multidisciplinary sciences owing to rapid development of their optimized structural properties. On the other hand, miniaturization of materials for nanotechnology recently requires the use of electron microscopy assisted processing on the corresponding materials. However, it should be noted that *irradiation damage*, caused by the use of beams in the electron microscopes leads to undesired physical/chemical material property changes or uncontrollable modification of structures that are being processed. Nevertheless, it is well possible to turn degradation dependent physical/chemical changes from negative to positive use intentionally at the nanoscale, when electron microscopy is in charge for surface modification for creating functional surfaces. FIB/SEM platforms are capable of performing maskless site-specific structuring which are considered to be the major advantages of FIB over electron beam lithography.

The current work mainly focuses on optimization and modification of surface properties of Melinex<sup>®</sup> (polyester-PE) films via the use of electron and ion beam etching and XeF<sub>2</sub> gas assisted beam bombardment in a controlled way. The purpose is the development of functional etched and fluorinated surfaces on polymeric materials such as non-wettability / non-adhesiveness and electrical/optical characteristics, using electrons/ions and assistant gases; and accordingly, novel materials are to be designed for diverse nanotechnologies including medicine, pharmaceuticals and electronics. For the experiments, different instrumental parameters; such as: varying current values, exposure times, irradiation modes and etching rates were applied on the targeted surfaces. The alterations in the surface properties provided by surface modification processes performed in FIB-SEM dual-beam platforms were tracked by SEM imaging, AFM measurements, Raman spectral analysis and EDS investigations.

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## P-25: Ab initio studies of the fragmentation of $(\text{PMe}_3)\text{Ag}(\text{PMe}_3)$

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Focused Electron Beam Induced Deposition FEBID still has to live up to the original idea of providing a tool for electron-controlled chemistry on the nanometer scale [1]. This has to be understood in the sense that, by providing a suitable environment during the FEBID process, the outcome of the electron-induced reactions can be steered in a controlled way towards yielding the desired composition of the products. However, this new technology relies on precursors that are not optimized for the electron driven process. The selection of the appropriate precursor can be challenging. Botman et al. highlight the difficulty in depositing pure metals [2], but more challenging is the lack of volatile precursor compound for silver.

The aim of our study is to show that  $\text{Ag}(\text{PMe}_3)_2$  could be used as a precursor for FEBID. In this sense, the thermal and chemical stability, toxicity, electronic structure and energy of appearance of the Ag derivatives from the neutral and differently charged  $(\text{PMe}_3)\text{Ag}(\text{PMe}_3)$  molecule were investigated. A theoretical method was used to predict the most favorable fragmentation channels according to the lowest appearance energy. Referring to results obtained, the most favorable channel lead to formation of the positively charged Ag atom and two neutral fragments of  $\text{PMe}_3$  (Table 1).

Table 1. Energy of appearance of the variously charged fragments Ag and  $2*\text{PMe}_3$

Ag charge	$2*\text{PMe}_3$ charge	Energy of appearance, eV
-1	-1	14.43
-1	0	8.44
-1	1	14.43
0	-1	7.63
0	0	1.64
0	1	7.63
1	-1	6.93
1	0	0.94
1	1	6.93

[1] M. Huth, F. Porrati, Ch. Schwalb, M. Winhold, R. Sachser, M. Dukic, J. Adams, G. Fantner, *Beilstein J Nanotechnol.* **3** (2012) 597.

[2] A. Botman, J. Mulders, C. Hagen, *Nanotechnology* **20** (2009) 372001.

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## P-26: Computational study of dissociative electron attachment to $\pi$ -allyl ruthenium (II) tricarbonyl bromide

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Understanding the interactions of organometallic compounds with low energy electrons, is considered vital to the field of focused electron beam induced deposition (FEBID).<sup>1</sup> To this end, studies of dissociative electron attachment (DEA) to the organometallic compound  $\pi$ -allyl ruthenium (II) tricarbonyl bromide have previously been performed and energy thresholds have been measured for the yields of eight ionic fragments. This poster presents the results of a study wherein a theoretical protocol is established for the accurate calculation of thermochemical threshold energies for DEA on this organometallic complex. Several computational methods including density functional theory (DFT), hybrid-DFT and a coupled cluster method were evaluated for their ability to predict these threshold energies. Density functional theory and hybrid DFT methods were surprisingly found to have poor reliability in the modelling of several DEA reactions; however, the coupled cluster method LPNO-pCCSD/2a was found to produce much more accurate results. Using the local correlation pair natural orbital (LPNO) methodology, high level coupled cluster calculations for open-shell systems of this size are now affordable, paving the way for reliable theoretical DEA predictions of such compounds.

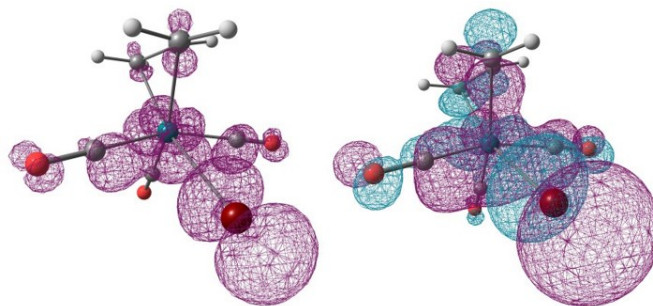


Fig. 1. Spin density isosurface (left) and SOMO isosurface (right) of  $\pi$ -allyl ruthenium tricarbonyl bromide anion, calculated with a contour value of 0.025000.

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[1] I. Utke, P. Hoffmann and J. Melngailis, *J. Vac. Sci. Tech. B: Microelectronics and Nanometer Structures* **26** (2008) 1197.

## P-27: Electron collisions with methyl-substituted ethylenes

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Understanding physical, among others, phenomena accompanying the interaction of charged particles with matter requires comprehensive information about the total cross sections for electron collisions with polyatomic molecules. In addition, information about the collisions of electrons with the particles is essential in modeling and controlling the physico-chemical reactions.

The total cross section (TCS), containing complex information from all scattering channels, is a quantity, which can be determined with good accuracy without any normalization procedures. Due to its reliable absolute value, the experimental TCS can be used as a calibration standard or upper limit reference for the normalization of cross sections for particular processes, as well as for the estimation of scattering quantities, which are difficult to obtain. The TCS data also may test the reliability of theoretical models and computational procedures used in the electron-scattering calculations. However, in spite of unceasing interest in the electron-driven processes for media containing hydrocarbons, there is still a need to gather the data for more complex compounds.

The main goal of this work is to provide the electron-scattering absolute data for larger methyl-ethylenes [1]. The total cross section (TCS) absolute values for the electron scattering from 2-methyl-2-butene and 2,3-dimethyl-2-butene are measured from 0.5 to 300 eV in the linear electron-transmission experiment. Furthermore, having in hand the electron-scattering TCS data for the C<sub>2</sub>H<sub>4</sub> molecule and for the family of its methylated derivatives (C<sub>n</sub>H<sub>2n</sub>; n = 3–6), we examine how the replacement of hydrogen atoms with the CH<sub>3</sub> group reflects in the cross section. Finally, to investigate if the arrangement of atoms in the examined target molecules affects the TCS behavior, we compare the present data for 2-methyl-2-butene and 2,3-dimethyl-2-butene with those available for their isomeric counterparts 1-pentene and cyclohexane, respectively.

[1] Cz. Szmytkowski, S. Stefanowska, M. Zawadzki, E. Ptasińska-Denga and P. Możejko, *J. Chem. Phys.* **143** (2015) 064306.

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