

# Chemistry for ELectron-Induced Nanofabrication - CELINA

## COST Action CM1301

COST Action CM1301 (CELINA) is now looking forward to its third annual meeting to be held during May 18-20, 2016 in Krakow. One particular focus of this meeting will be to discuss how the precision and versatility of FEBID can profit from combination with thermal surface chemistry. CELINA thus links up with COST Action **HERALD (Hooking together European research in atomic layer deposition)** and has invited the Chair of HERALD, Simon Elliott from the University College Cork, to give us an *Introduction to Atomic Layer Deposition and the COST Action HERALD*. As another invited speaker, Erwin Kessels from Eindhoven University of Technology will particularly review the links of ALD with FEBIP. Electron beam induced surface activation and chemical selectivity as new routes for the fabrication of well-defined nanostructures will be discussed by Hubertus Marbach.

The combination of electron-induced and thermal chemistry is a theme also inherent in deposit purification processes that have repeatedly been addressed during recent Short-term Scientific Missions (STSMs) within CELINA. Developing und understanding such purification processes is thus an important area of research and impressive successes have recently been achieved in this area. A small workshop on **Perspectives of carbon-containing FEBID precursors**, held in Bremen on March 1, 2016, has revealed that much remains to be investigated in this area of FEBID research but, if successful, such purification processes can enable a targeted approach for the development of better FEBID precursors by using or modifying readily available CVD precursors.

The momentum that CELINA has gained by now is also underlined by a major increase in STSMs, too many actually to be all listed in this newsletter which thus restricts itself to a representative selection of subjects. However, you are warmly invited to visit our website to find all the information there. This has also been done by our 2014 external expert Lisa McElwee-White from the University of Florida at Gainesville. Lisa has put tremendous effort recently into reviewing for COST the past and ongoing activities of CELINA. **A big thank you to Lisa!!!**



The city of Krakow welcomes CELINA for its third annual general Meeting

*COST Action CELINA chair*  
*Petra Swiderek*

*COST Action CELINA vice-chair*  
*Cornelis W. Hagen*

*COST Action CELINA STSM manager*  
*Nigel Mason*

*WG1*  
*Electron-induced reactions of FEBID precursors*  
Chair: Janina Kopyra  
Vice-chair: Oddur Ingolfsson

*WG2*  
*Synthesis of novel FEBID precursors*  
Chair: Sven Barth  
Vice-chair: Patrik Hoffmann

*WG3*  
*Application of novel precursors in the FEBID process*  
Chair: Ivo Utke  
Vice-chair: Roser Valenti

*Highlight publications from CELINA – must read!*  
*- The Action Chair's selection -*

**A recent review from Iceland in collaboration with our international partner Howard Fairbrother gives an up-to-date summary of electron-induced fragmentation processes in FEBID precursors:**

*The role of low-energy electrons in focused electron beam induced deposition: four case studies of representative precursors*, R.M. Thorman, Ragesh Kumar T.P., D.H. Fairbrother, O.Ingólfsson, Beilstein J. Nanotechnol. (2015) 6, 1508–1517.

**A collaborative study between the Innsbruck and Lisbon groups has revealed a surprising yield of bare metal dimer ions upon electron impact ionization of Van der Waals aggregates of  $W(CO)_6$ :**

*Complete ligand loss in electron ionization of the weakly bound organometallic tungsten hexacarbonyl dimer*, M. Neustetter, A. Mauracher, P. Limão-Vieira, S. Denifl, Phys. Chem. Chem. Phys. (2016) 18, 9893-9896.

**Recent work from Prague and from collaborations of the same group with Belgrade and Fribourg reveals that electronic excitation in aggregates of precursor molecules dissipates excess energy and should also not be neglected as efficient fragmentation mechanism in FEBID:**

*Self-scavenging of electrons in  $Fe(CO)_5$  aggregates deposited on argon nanoparticles*, J. Lengyel, J. Kočišek, M. Fárnik, J. Fedor, J. Phys. Chem. C (2016) 120, 7397-7402.

*Excited States of  $Pt(PF_3)_4$  and Their Role in Focused Electron-Beam Nanofabrication* M. Zlatar, M. Allan, J. Fedor, J. Phys. Chem. C (2016), DOI:10.1021/acs.jpcc.6b02660.

**Is  $NH_3$  a favourable ligand for FEBID precursors? This has been studied jointly by CELINA groups in Bremen, Thun, and Groningen:**

*Role of  $NH_3$  in the Electron-Induced Reactions of Adsorbed and Solid Cisplatin*, J. Warneke, M. Rohdenburg, Y.C. Zhang, J. Orzagh, A. Vaz, I. Utke, J.T.M. de Hosson, W.F. van Dorp, P. Swiderek, J. Phys. Chem. C (2016) 120, 4112-4120.

**An article from the international FEBID community gives a good overview of potential advantages and present developments in applying non-volatile precursors:**

*Rapid electron beam writing of topologically complex 3D nanostructures using liquid phase precursor*, J.S. Fisher, P.A. Kottke, S. Kim, A.G. Fedorov, Nano Lett. (2015) 15, 8385-8391.

**As an interesting application, FEBID has been proposed as an efficient method to make superior contacts between graphene and metal electrodes:**

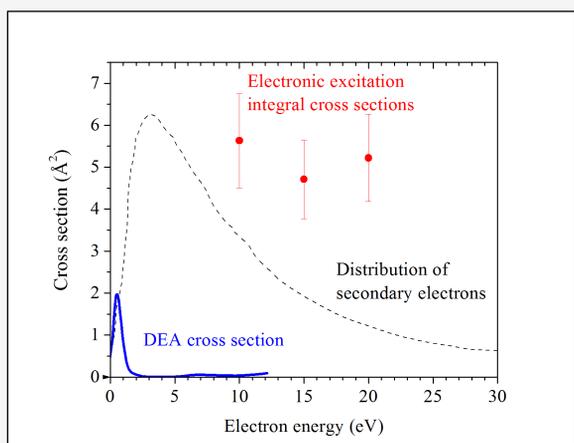
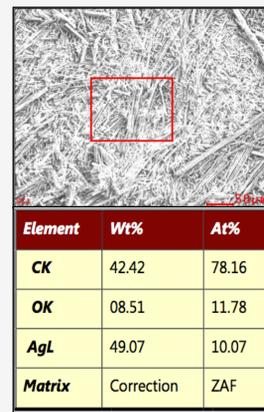
*Activating “invisible” glues: Using electron beam for enhancement of interfacial properties of graphene-metal contact*, S. Kim, M. Russell, D.D. Kulkarni, M. Henry, S. Kim, R.R. Naik, A.A. Voevodin, S.S. Jang, V.T. Tsukruk, A.G. Fedorov, ACS Nano (2016) 10, 1042-1049.

More publications from CELINA can be found on our website. Please always remember to send your new publications to the Chair!

## News from the STSMs

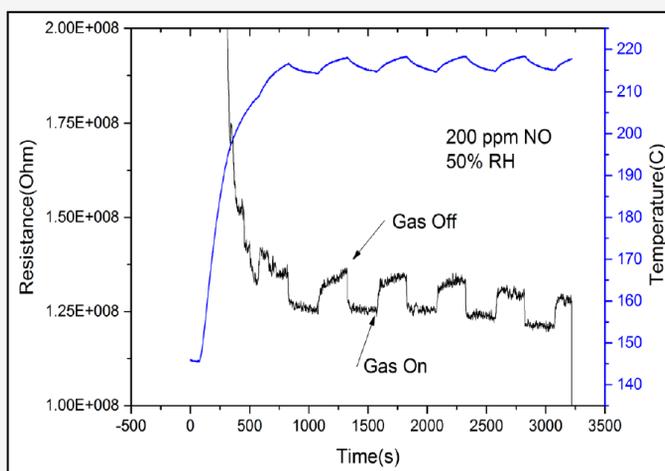
Short-term scientific missions (STSMs) provide excellent opportunities to establish new collaborations but also to use facilities throughout Europe and to pursue new ideas before they are funded on a larger scale. Through STSMs, CELINA establishes links between the scientific communities as assembled in the three WGs. Some selected recent achievements are highlighted here.

Precursors with only few ligands bear the promise of being easy to decompose. However, they do not necessarily have sufficient vapour pressure to be used in a standard FEBID process. Therefore, a new gas inlet system consisting of an evaporator located close to the beam focus has been developed at EMPA in Thun (CH). During an STSM to this lab, **Katja Höflich** from the Helmholtz Centre Berlin for Materials and Energy (DE) conducted tests to verify if several precursors for silver deposition, among them one provided by the group of Heinrich Lang in Chemnitz (DE) can be introduced using this new equipment and favourably decomposed under electron irradiation. Among them, Ag-dimethylbutyrate can, in fact, be evaporated intact (see figure) and the majority of the ligand material can then be removed by the electron beam.



The role of neutral excited states in fragmentation of FEBID precursors has so far rarely been investigated. As experimental evidence in this respect is still sparse, support from theory is very important. To shed light on this problem, **Juraj Fedor** from the Heyrovsky Institute of the Academy of Sciences in Prague (CZ) visited Matija Zlatar at the University of Belgrade (RS) to participate in a computational study of different electronic states of  $\text{Pt}(\text{PF}_3)_4$ . Combined with available experimental data on the cross sections for dissociative electron attachment (DEA) and electronic excitation of this precursor, the theoretical study leads to the striking result that electronic excitation may contribute even more strongly to fragmentation in FEBID processes than DEA. This is highly important because so far, DEA has been thought to be the most important initial step in precursor decomposition.

Bimetallic deposits are of interest because they bear the potential that their properties can be tuned by varying the composition. An STSM performed by **Aleksandra Szkudlarek** from the AGH University of Science and Technology in Krakow (PL) aimed at such materials with the aim to investigate their performance in sensing applications. In particular, nanogranular materials with different composition were produced at EMPA in Thun (CH) by fabricating FEBID deposits using  $\text{Cu}(\text{hfac})_2$  and  $\text{Me}_2\text{Au}(\text{acac})$  as precursors. Monometallic Cu and Au deposits as well as bimetallic structures were produced. By post-deposition annealing, these materials can be transformed to a conductive state and can be tested with respect to their sensing response.



## *Short Term Scientific Missions – STSMS*

STSMS allow participants to make visits to labs in another participating country to initiate new collaborative projects or elaborate promising developments. Detailed information on the application process is listed on the CELINA webpage.

A total number of 34 STSMS were granted during the last 9 months including contributions from all 3 WGs and involving 15 of the participating countries. The projects performed during the STSMS ranged from fundamental studies on electron-induced precursor fragmentation to work aiming at the fabrication of improved nanoscale devices and included also the development of theoretical approaches to processes involved in FEBID. A list of all STSMS performed recently can be found on the CELINA website.

## *Upcoming events*

### CELINA 2016

The third meeting of COST Action CM1301

Location: Krakow, Poland

Date: May 18-20, 2016

Jointly with the fifth Meetings of Working Groups 1, 2, and 3 of CELINA.

[Conference homepage](#)

### **1st International Conference on Helium Ion Microscopy and Emerging Focused Ion Beam Technologies (HEFIB 2016)**

Location: Luxembourg City

Date: June 8-10, 2016

[Conference homepage](#)

### **6th Workshop on Focused Electron Beam Induced Processing (FEBIP 2016)**

Location: Vienna, Austria

Date: July 5-8, 2016

[Conference homepage](#)

Sixth meetings of Working Groups 2 and 3

Location: Vienna, Austria

Date: to be announced

Jointly with the 6th Workshop on Focused Electron Beam Induced Processing (FEBIP 2016)

More information following...

FEBIP 2016 will also host a CELINA training school with sessions on precursor properties and handling, fundamental electron-induced processes and experimental approaches to their study, as well as sessions on the simulation of FEBID processes and practical aspects of performing FEBID. More information will be released soon. Check out the CELINA website!