Chemistry for ELectron-Induced Nanofabrication - CELINA
COST Action CM1301

CELINA looks back to a successful first year with meetings in Erlangen, Frankfurt, and Belgrade, new collaborations, interesting new precursors, some surprises about old precursors and a total of already 20 short term scientific missions, among them 8 performed by female ESRs! We now have funds ready to start into an equally stimulating second year. The present CELINA newsletter gives an overview of the upcoming events but also highlights some of the exciting results obtained during the first year. We hope you enjoy reading it.

Highlight publications from CELINA – must read!

- The Action Chair's selection -

- A contribution from our industry partners at Carl Zeiss SMS GmbH discusses, among others, potential material needs for future development of FEBID technology: *Industrial perspective on focused electron beam-induced processes* - Tristan Bret, Thorsten Hofmann, Klaus Edinger, Appl. Phys. A (2014) 117, 1607-1614.

- Gas-phase studies from the University of Iceland identify a silicon precursor with negligible DEA cross section which might of use to monitor the action of secondary electrons in FEBID: *Dissociative electron attachment and dissociative ionization of 1,1-dichloro-1-silacyclohexane and silacyclohexane*, - Elías H. Bjarnason, Benedikt Ómarsson, Nanna Rút Jónsdóttir, Ingvar Árnason, Oddur Ingólfsson, Int. J. Mass Spectrom. 370 (2014) 39-43.

- The He ion beam microscope may serve as tool for nanoscale deposition with improved spatial resolution: *Focused helium-ion-beam-induced deposition* - P.F.A. Alkmade, H. Miro, Appl. Phys. A (2014) 117, 1727-1747.

- Water can be used to rehabilitate the notoriously 'bad precursor' $MeCpPtMe_3$: *Rapid and highly compact purification for focused electron beam induced deposits: A low temperature approach using electron stimulated H_2O reactions* - Barbara Geier, Christian Gspan, Robert Winkler, Roland Schmied, Jason D. Fowlkes, Harald Fitzek, Sebastian Rauch, Johannes Rattenberger, Philip D. Rack, Harald Planck, J. Phys. Chem. C (2014) 118, 14009-14016.

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

Upcoming events

Forth meeting of Working Group 1
Location: Lisbon, Portugal
Date: during July 17-20, 2015
Jointly with the POSMOL 2015
http://eventos.fct.unl.pt/posmol2015/home

Forth meeting of Working Group 2
Location: Sempach, Switzerland
Date: during July 13-17, 2015
Jointly with the Euro-CVD 20
http://eurocvd20.empa.ch

Forth meeting of Working Group 3
Location: The Hague, Netherlands
Date: during September 21-24, 2015
Jointly with the MNE 2015
http://mne2015.org

CELINA 2015
The second meeting of COST Action CM1301
Location: Bratislava, Slovakia
Date: May 6-9, 2015
Jointly with the third Meetings of Working Groups 1, 2, and 3 of CELINA.
http://neon.dpp.fmph.uniba.sk/celina2015

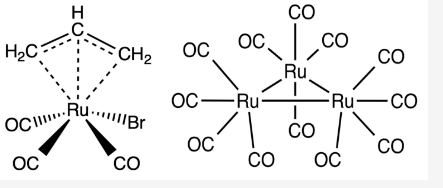
EIPBN 2015
The 59th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication
Location: San Diego, California
Date: May 26-29, 2015
http://eipbn.org

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

News from the STSMs

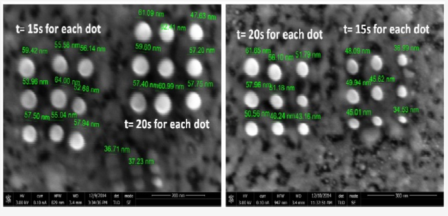
CELINA aims at linking different scientific communities as assembled in the three WGs. STSMs performed during the first year of the Action have made major contributions towards this aim including several that have established new collaborations across the WGs. Several examples shall highlight the recent achievements.

Rachel Thorman from the University of Iceland (IS, WG1) visited EMPA Thun (CH, WG3) to perform, among others, a study on the performance of the novel precursor $RuC_3H_5(CO)_3Br$. Deposit with C:Ru ratio as low as 1:1 were achieved in contrast to a ratio of 2:1 obtained with the known precursor $Ru_3(CO)_{12}$. Together with gas phase results obtained at the University of Iceland and surface science data contributed by our external partner Howard Fairbrother at John Hopkins University (US), the following picture emerges. $RuC_3H_5(CO)_3Br$ readily loses CO upon low energy electron exposure also contributing to precursor decomposition by secondary electrons (SEs) in the FEBID process. According to surface science experiments also, Br can at least in part be removed. Interestingly, the particularly low carbon content indicates that the allyl ligand can be degraded as well.



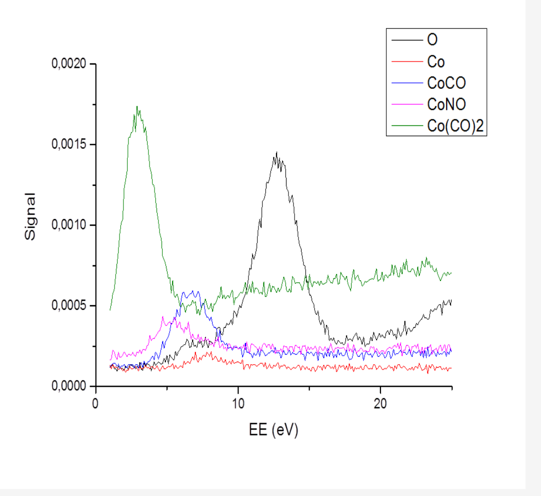
$RuC_3H_5(CO)_3Br$ (left) and $Ru_3(CO)_{12}$ (right)

During an STSM at the Technical University Delft (NL, WG3) **Ragesh Kumar,** equally from the University of Iceland examined the role of dissociative electron attachment (DEA) and dissociative ionization (DI) in determining the resolution of FEBID structures by comparing the performance of precursor molecules 1,1-dichloro-1-silacyclohexane, silacyclohexane and 1,3,5-trisilacyclohexane. Gas phase experiments had revealed that both 1,1-dichloro-1-silacyclohexane and silacyclohexane exhibit DI channels, but while 1,1-dichloro-1-silacyclohexane is sensitive to DEA as well, DEA in silacyclohexane is inefficient. As the chemistry of FEBID is thought to be driven to a large extent by low energy SEs, the idea behind this study was that molecules that are insensitive to DEA might form higher resolution structures than those that exhibit both DEA and DI channels. These could then be developed as FEBID precursors for high resolution work. As can be seen here, the proximity effect is in fact considerably more important for 1,1-dichloro-1-silacyclohexane than for silacyclohexane. This suggests that the absence of DEA channels might be significant in achieving high resolution deposits. Further experiments are planned to confirm this.

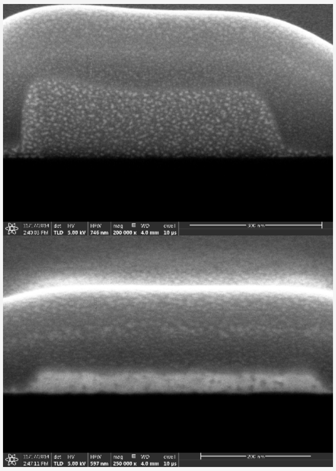


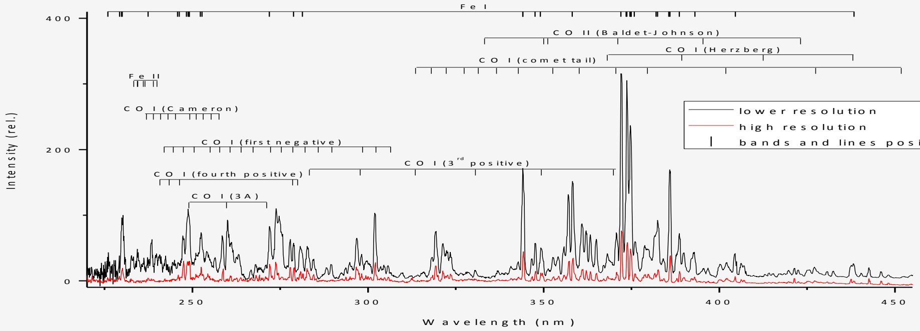
Array of nanopillars deposited with a) silacyclohexane and b) 1,1-dichloro-1-silacyclohexane to study the proximity effect

The effect of the condensed environment can considerably alter the electron-induced chemistry of precursors when going from the gas phase to the real FEBID process. To unravel such effects, **Andrew Ellis** from the University of Leicester (UK) performed studies on the electron-induced decomposition of $Co(CO)_3NO$ in liquid helium nanodroplets at the University of Innsbruck (AT). $Co(CO)_3NO$ is one of the prototypical FEBID precursors and has been used for controlled deposition of metallic cobalt. An important challenge is to understand the role of dissociative attachment induced by SEs. To extract new information on the mechanisms, controlled electron addition to $Co(CO)_3NO$ has been carried out inside liquid helium nanodroplets. With the rapid cooling available in helium droplets it should be possible to quench and identify specific reaction intermediates which are not observable in the gas phase because of fast secondary reactions. Another aspect to this work was to explore how the mechanism might be altered on a solid surface, and in this case C_{60} was chosen as the model surface. The image shows how the yield of certain fragment anions varies with electron energy (EE). Analysis of these and other data, including studies of $Co(CO)_3NO$ on C_{60}, reveal significant differences from previous gas phase measurements thus yielding promising new information on the role of SEs in the decomposition of a typical FEBID precursor.



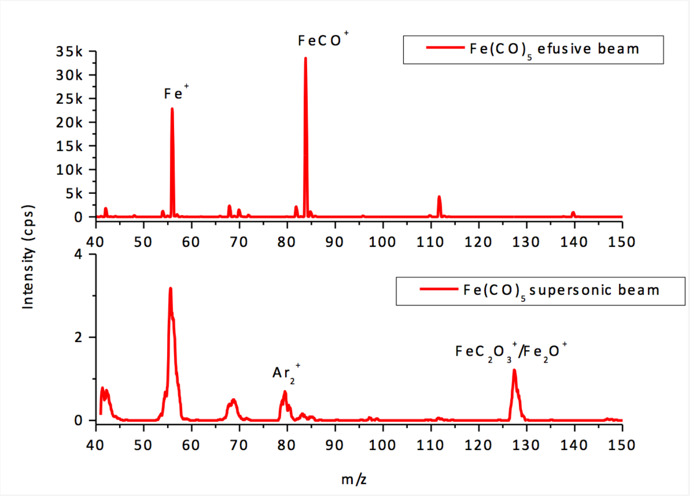
The purification of Gold Deposits using Me_2(acac) and oxygen was the aim of an STSM to FEI in Eindhoven(NL) by **Patricia Peinado** from the University of Zaragoza (ES). The use of carbon-based precursors during an EBID process usually leads to a deposit containing not only the metal we are aiming to obtain but also a high content of carbon. This is undesirable for electrical applications since the resistivity of these deposits is extremely low compared to pure metal. In order to avoid this problem, a flux of oxygen was used to help the carbon to escape from the structure in the form of CO or CO_2 molecules. The experiments showed that it is possible to control the current, voltage and dimensions at which the deposits grow by selecting an appropriate flux of oxygen to purify the structure. Also, oxygen treatments after and during deposition were compared. The two images show the difference between an untreated gold deposit (top) and a purified structure (bottom).





Emission spectrum ar 50 eV incident electron energy and 200 μm and 100 μm slits with determined lines and bands. (left)

The electron-induced fragmentation reactions of $Fe(CO)_5$ is addressed at Comenius University in Bratislava (SK) using a wide range of gas phase and cluster experiments. Two STSMs have contributed to this project. **Jaroslav Kocisek** from Jan Heyrovsky Institute of Physical Chemistry in Prague (CZ) conducted experiments using a molecular beam produced from a supersonic expansion of Ar/Fe(CO)5 mixtures. The resulting clusters were studied by electron impact ionization. The obtained mass spectra suggest that formation of degradation products containing more than one Fe atom can be monitored using this technique. **Filipe Ferreira da Silva** from Universidade Nova de Lisboa (PT) has tackled the problem of detecting neutral fragments by use of a setup allowing to measure electron-induced fluorescence. This way, also neutral fragments resulting after electron impact such as atomic Fe and molecular CO can be accounted for in the gas phase thus giving access to these often evasive products.



Comparison of gas phase mass spectra (top) and cluster mass spectra (bottom) of $Fe(CO)_5$ obtained at an electron energy of 70eV

Esther Carrasco from the University of Erlangen (WG3, DE) equally visited a partner from WG1 at Instituto de Física Fundamental (CSIC) in Madrid (WG1, ES) to perform electron irradiation studies on carbon precursors adsorbed on Si substrates. This STSM has initiated a new approach to carry out combined experimental and theoretical studies of electron induced processes in connection with FEBIP. Irradiation experiments on a new suitable set-up will provide the energy and angular distribution of the generated secondary species to be compared with the simulated ones supplied by an event by event Monte Carlo code. The aim is to evaluate Monte Carlo models as a potential tool for electron beam induced deposition techniques and to provide further fundamental insight into the initial steps of FEBIP.

Short Term Scientific Missions – STSM

STSMs allow participants to make visits to labs in another participating country to initiate new collaborative projects. CELINA now calls for applications for STSMs to take place in 2015. Detailed information on the application process is listed on the CELINA webpage.

Applicant	Host	Project	Dates
A Ellis University of Leicester (UK)	P Scheier University of Innsbruck (AT)	Mechanism of FEBID precursor deposition	15/09/14 25/09/14
J Maljkovic Institute of Physics, Belgrade (RS)	P Papp Comenius University in Bratislava (SK)	Electron impact dissociative ionization of tetraethyl orthosilicate	15/09/14 30/11/14
A Solov'yov MBN Research Center, Frankfurt am Main (DE)	A Fernández Inst de Ciencia de Materiales de Sevilla, (ES)	Application of MBN Explorer software package for deposition processes modeling	09/07/14 13/05714
A Laikhtman Holon Institute of Technology, (IL)	M Sezen Sabanci University, (TR)	Study of electron and ion-surface interactions in inorganic nanomaterials using focused electron and ion beams	15/10/14 2310/14
R Kumar University of Iceland, (IS)	C W. Hagen Delft University of Technology, (NL)	Relative role of DEA and DI on FEBID nanostructure	16/09/14 30/11/14
J Warneke University of Bremen, (DE)	I Utke EMPA, Swiss Federal Institute of Materials Testing and Research, (CH)	Electron induced decomposition of cis-platin	13/10/14 18/10/14
P Peinado INA, (ES)	H Mulders FEI, (NL)	Optimization of Gold deposits with FEBID	06/10/14 30/11/14
J Sama Universitat de Barcelona, (ES)	P Trompenaars FEI Electron Optics,(NL)	Purification of electron assisted Pt deposition for nano gas sensor devices	02/11/14 08/11/14
A Romano-Rodriguez Universitat de Barcelona, (ES)	Ivo Utke EMPA Switzerland, CH)	Purification of electron assisted Pt depositions for nano gas sensor devicees	02/11/14 08/11/14
A Szkudlarek Academic Centre for Materials and Nanotechnology AGH, (PL)	I Utke EMPA Switzerland, CH)	Systematic study of thermal purification of copper FEBID deposits	07/11/14 25/11/14
M Kamerbeek Delft University of Technology, (NL)	A Goodyear Oxford Instrument Plasma Technology Lab, (UK)	Nano-pattern transfer into Silicon using etch masks made by Electron Beam Induced Deposition	17/11/14 21/11/14
M Scotuzzi Delft University of Technology, (NL)	A Goodyear Oxford Instrument Plasma Technology Lab, (UK)	Nano-pattern transfer into Silicon using etch masks made by Electron Beam Induced Deposition	17/11/14 21/11/14
K Höflich Helmholtz Centre Berlin for Materials and Energy, (DE)	I Utke EMPA Switzerland, CH)	Test of Novel Precursors for Copper and Silver Deposition	19/11/14 28/11/14