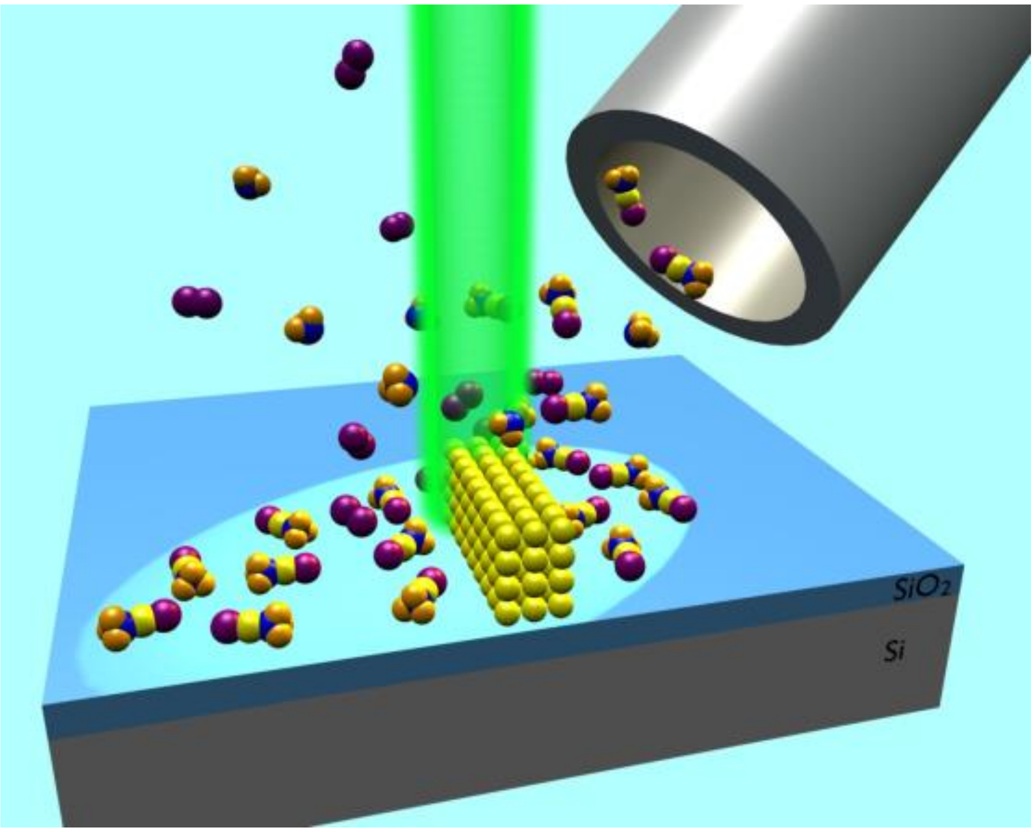
CELINA

Chemistry for **EL**ectron-**I**nitiated **NA**nofabrication



COST Action CM1301 CELINA
2013-2017

Map showing national partners of CELINA.

CELINA is a COST (European Cooperation in Science and Technology) Action created under the Chemistry and Molecular Sciences and Technologies panel *(CM1301) to run for four years (2013-17). It has…*

…engaged more than 130 scientists from
24 COST countries and
5 non-COST partners (Australia, Canada, India, USA)
with 7 industrial partners

…supported more than 60 scientific exchanges

…published more than 70 papers

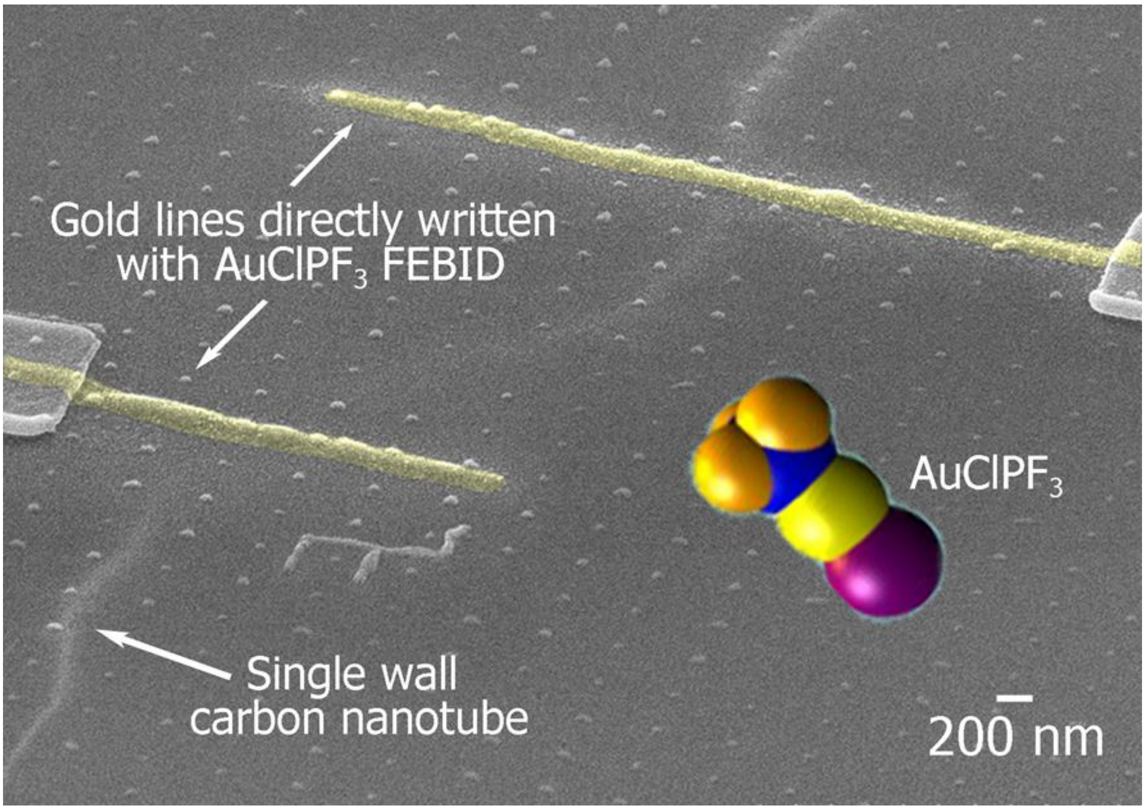
…organised or contributed to 11 scientific workshops and conferences

http://celina.uni-bremen.de/celina/

CELINA's Objectives

The COST Action CELINA performs pioneering research that will gain a profound understanding of how electrons can be used as tool in nanofabrication. In particular, CELINA studies the fundamental electron-induced chemistry in gas phase and on surfaces that will improve the performance of **Focused Electron Beam Induced Deposition (FEBID)**. Building on this knowledge, new precursor molecules have been designed and synthesized to advance the performance of FEBID such that it can be exploited by the European nanotechnology industry. Europe is at the forefront of such research and is currently developing FEBID as a commercially viable technique which provides the stage for a range of collaborative projects supported by CELINA.

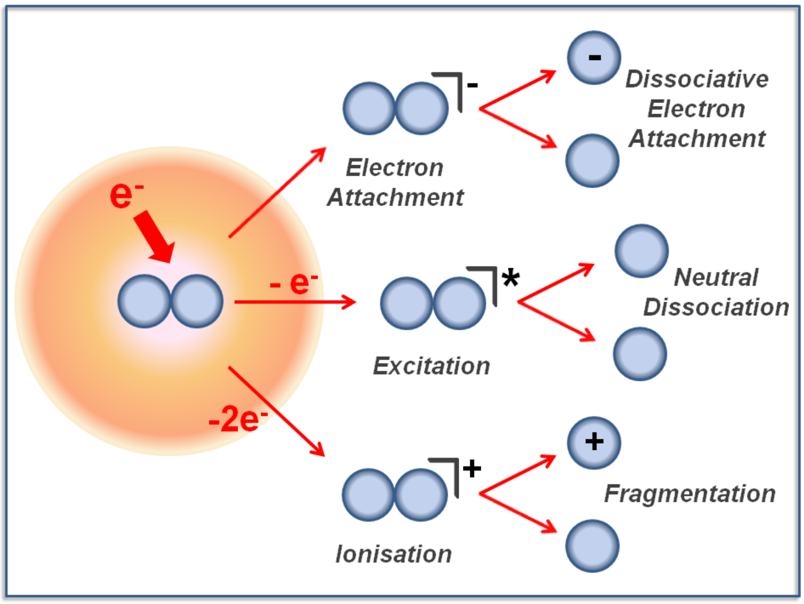
This booklet summarises the current state of the art in the field and the projects and collaborations that have been assembled to conduct this research programme.



Au lines fabricated by FEBID as contacts for the electrical characterization of a single carbon nanotube.
(from I.Utke, A.Gölzhäuser, Angew. Chem. Int. Ed. 2010, 49, 9328 – 9330).

How do electrons induce chemistry ?

Electrons transfer kinetic energy to internal energy within the molecule (AB) during **collisions** and thereby prepare molecules in different reactive states.



If the electron has a sufficiently high energy, this may lead to ionisation (AB^+) or fragmentation (A + B) of the molecule or a combination of both:

$$e^- + AB \rightarrow AB^+ + 2e^-$$
$$e^- + AB \rightarrow A + B + 2e^-$$
$$e^- + AB \rightarrow A^+ + B + 2e^-$$

A special type of collision process is that of *Dissociative Electron Attachment* (*DEA)* in which the colliding electron is temporarily attached to the molecule before either 'autodetaching' or inducing fragmentation. DEA occurs at electron energies well below the ionisation energy and often even below the bond energies that need to be overcome. It induces fragmentation of specfic bonds thus creating a product anion (A^-) and one or more neutral (reactive) species.

$$e- + AB \rightarrow A^- + B$$

The reactive fragments produced via these different types of electron collisions may also, in their encounters with other atoms or molecules, induce chemical reactions.

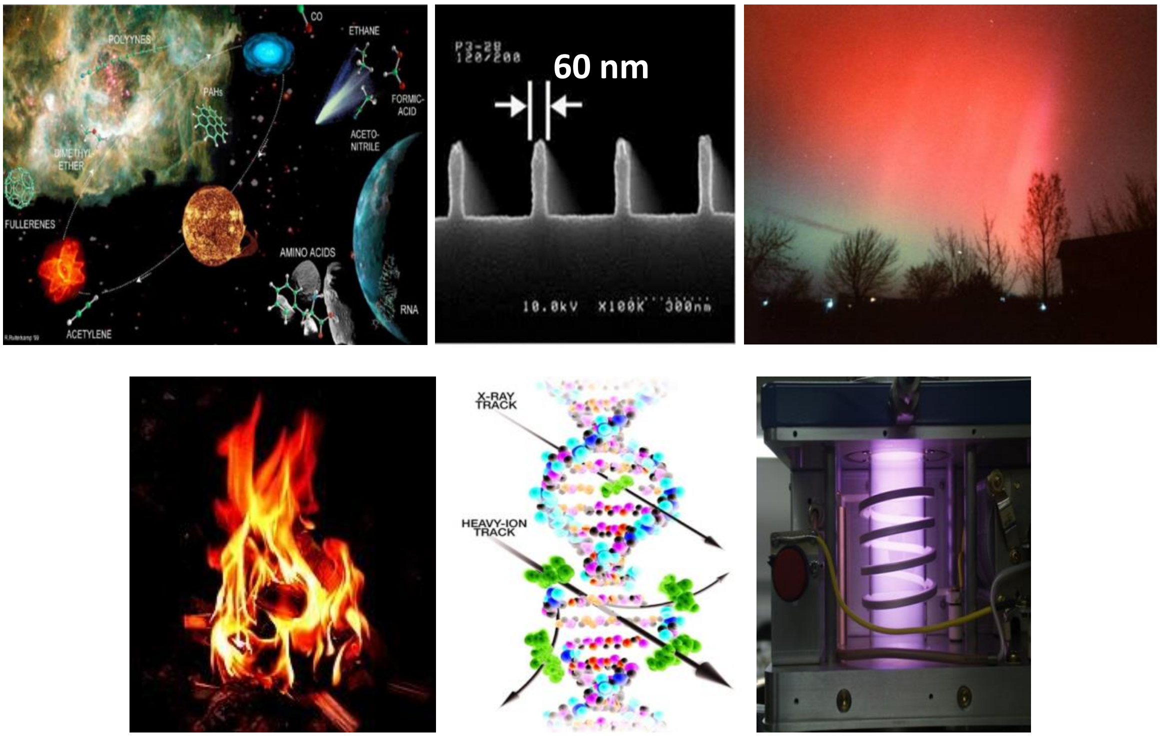
$$A + CD \rightarrow CAD$$

Hence by controlling the incident energy of the electons it is possible to select the bonds you wish to rupture and influence the chemistry in the local medium.

Electron induced Chemistry in science and technology

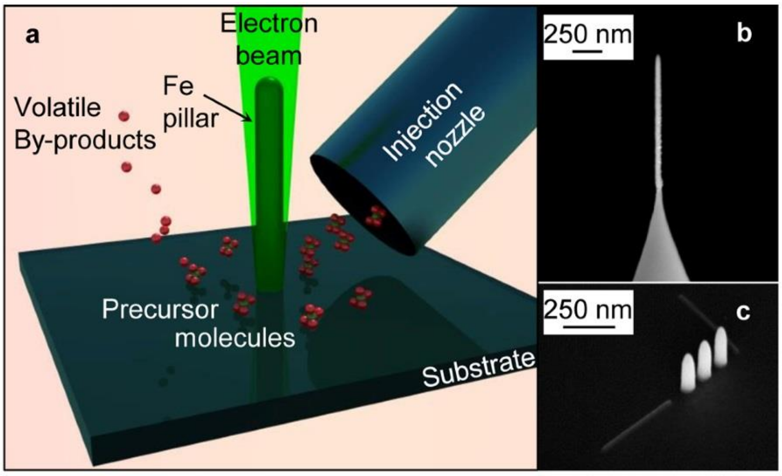
Electrons are ubiquitous and therefore collisions between electrons and molecules are prevalent in many natural phenomena. One of their most splendid displays is the aurora (on Earth and other planets). Electron-induced chemistry is now believed to play an important role in the synthesis of molecules in space with $C_xN_y^-$ and $C_xH_y^-$ anions being discovered in the interstellar medium. Low energy electrons are also able to rupture DNA and other large biomolecules with DEA being an important process in radiation induced damage of living cells.

Electron collisions, electron impact ionisation and DEA are also integral to a number of technologies. They create and sustain plasmas and determine their properties, which is exploited by modern industry for plasma treatment of materials, plasma-induced lighting and plasma torches for surgery and sterilisation. Plasmas for semiconductor processing have had perhaps the greatest impact pioneering the development of the microchip and modern silicon based electronics. However, with the increasing demand for ever-shrinking physical devices, novel nanofabrication techniques are needed. Electron collisions are again fundamental to those highly promising technologies including **F**ocused **E**lectron **B**eam **I**nduced **D**eposition (FEBID).



Examples of electron induced processes in nature and industry. From top middle counterclockwise; Fabrication of nanostructures, synthesis of molecules in interstellar medium, combustion, radiation induced damage in DNA as part of radiotherapy, plasma lighting and the aurora..

Focused Electron Beam Induced Deposition (FEBID)



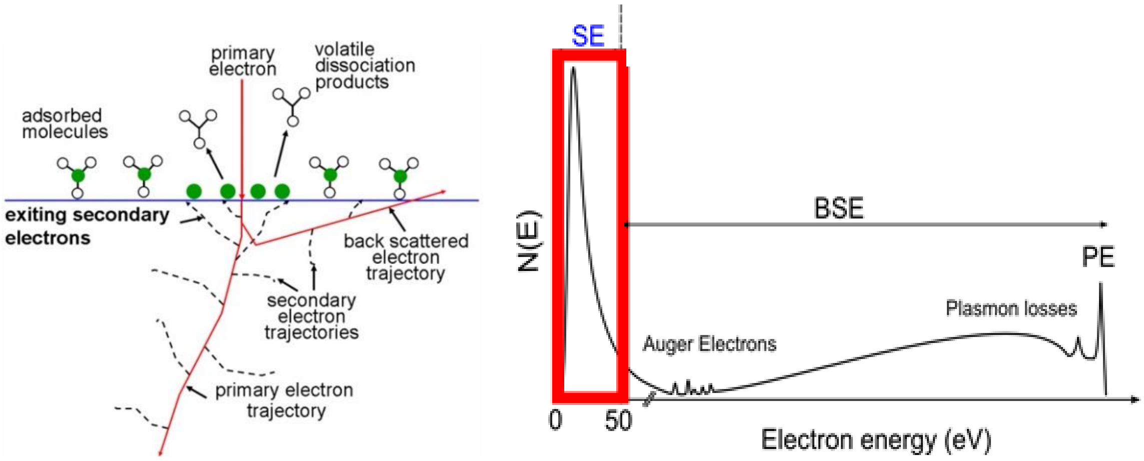
Schematic diagram of the FEBID process illustrating the formation of Fe-rich magnetic nanostructures using an $Fe(CO)_5$ precursor (from Gavagnin et al. ACS Appl. Mater. Interfaces 2014, 6, 20254–20260).

Focused Electron Beam Induced Deposition (FEBID) is a technique for producing structures on a surface with nanometre resolution. In FEBID a gaseous precursor is dissociated in the focus of a high energy (keV) electron beam while being deposited on the surface. The products of such electron induced processing (metals, oxides, carbon...) form deposits on the surface. As the electron beam is rastered over the substrate surface following a predefined pattern the deposits are built up to form complex 3D nanostructures.

In many instances and for a large variety of precursors the structures obtained by the FEBID process are formed by a composite consisting of metallic nanocrystals embedded in an insulating matrix. This has important consequences, for example such composites have significantly higher resistivity compared to that of the pure metal. Consequently, strong efforts are being made to improve on the metal content of FEBID structures with the ultimate goal of reaching 100% pure metal deposits necessary for nanoscale electronics.

These composites may have interesting physical properties e.g. hardness, approaching that of diamond or rubber-like behaviour in the pillars, depending on the precursor and process parameters. Hence it is necessary to optimise the precursor and electron irradiation for the required properties of the deposit.

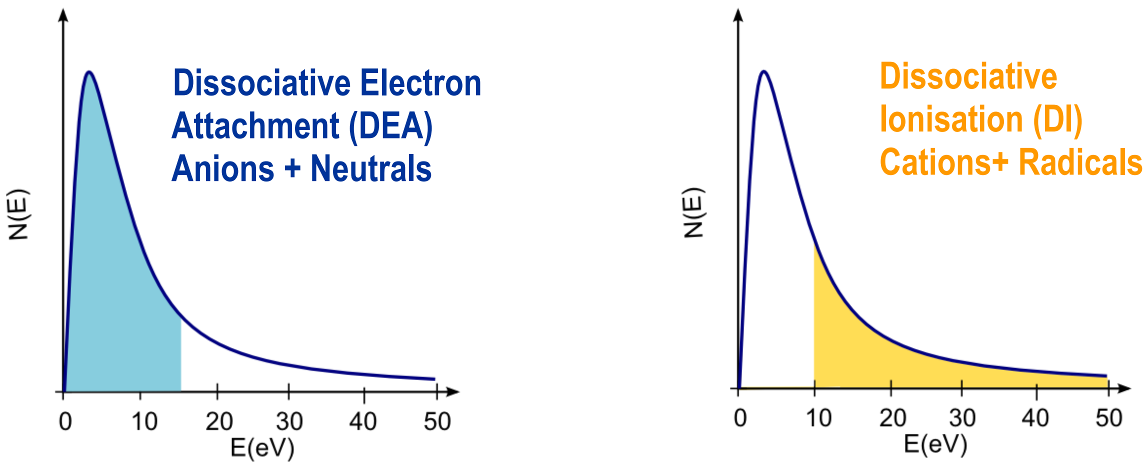
Electron processing in FEBID



Schematic representation of the primary electron entering the substrate (left) producing an avalanche of secondary electrons (SE) resulting in a continuous electron energy distribution (right).

If we are to understand the fundamental processes underpinning FEBID it is necessary to study electron interactions with the precursor molecules leading to the surface deposits that form FEBID fashioned structures. However, it is not only the primary electrons that are important since for every primary (keV) electron there are many secondary electrons produced.

The primary electrons may penetrate into the substrate or be backscattered losing energy such that the final electron distribution is a continuous function from primary electron to low energy (zero) thermalized electrons. Such an energy distribution overlaps with the maximum cross section for both electron-induced dissociative ionisation and dissociative electron attachment producing reactive species that drive FEBID chemistry. An important part of the CELINA programme is to study electron collision processes with FEBID precursors.

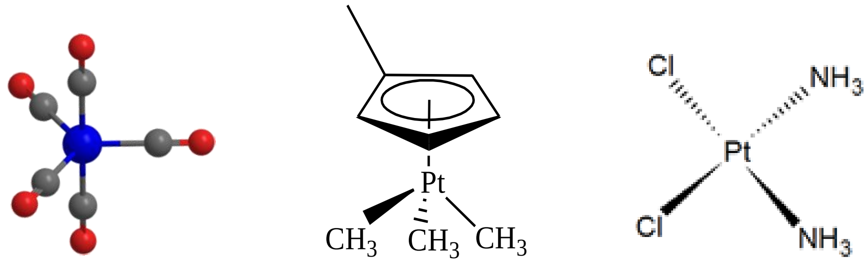


The energy regions in which secondary electrons induce molecular fragmentation.

Developing new precursors for FEBID

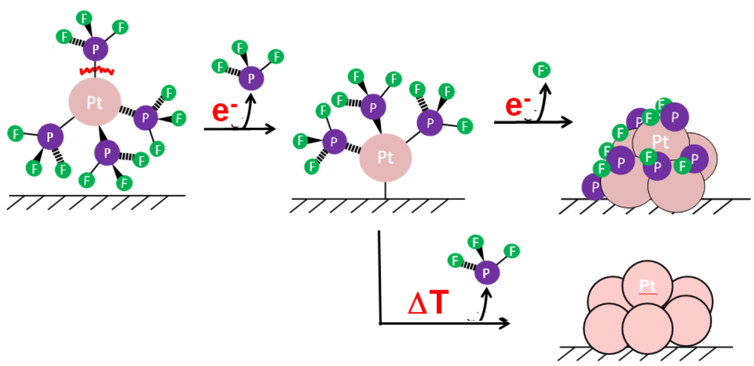
To date most FEBID precursor molecules have been drawn from existing compounds used in other surface fabrication processes (e.g. CVD). Hence commonly used compounds include $Fe(CO)_5$ and $Co_2(CO)_8$ but also molecules with larger side groups such as $MeCpPtMe_3$. CELINA, by bringing together synthetic chemists, collision physicists and FEBID engineers, has explored new FEBID precursors whose dissociation can produce pure metallic deposits.

Novel precursors specifically tailored for FEBID are being developed within CELINA. For example, bimetallic precursors such as $HFeCo_3(CO)_{12}$ serve as building blocks for the deposition of an Fe-Co alloy with predefined composition. However, to validate the favourable properties of specific ligands, compounds such as cisplatin, commonly used as a radiosensitizer in radiotherapy, are also investigated.



$Fe(CO)_5$ as a common precursor for Fe deposits with particular magnetic properties. The versatile and frequently used Pt precursor $MeCpPtMe_3$, and cisplatin, a well-known radiotherapy agent that may also be used in FEBID to build Pt structures with each of the groups attached to the central Pt atom removed by electron-precursor interactions.

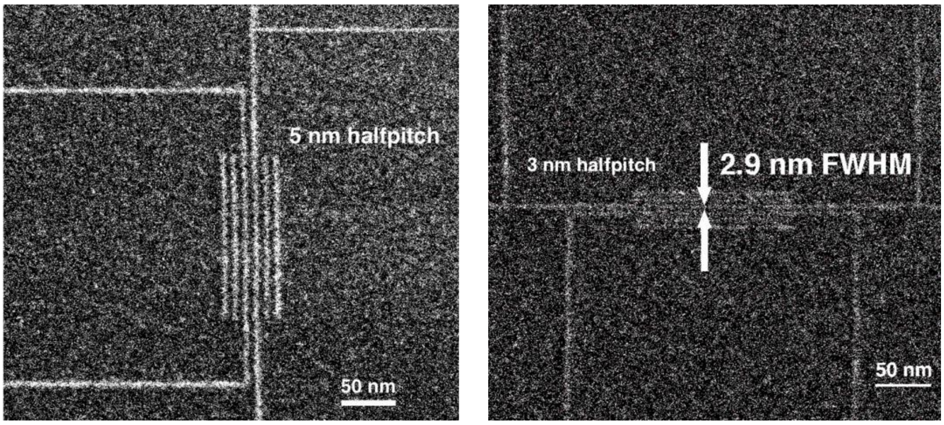
However, it is also important to explore not only electron-driven chemistry but also the effects of thermal and catalytic reactions in the dissociation of FEBID precursors. As an example, the purity of deposits fabricated from $Pt(PF_3)_4$ can be enhanced by working at an appropriate temperature.



Schematic of FEBID processing of $Pt(PF_3)_4$ to form deposits of pure Pt on the surface after post FEBID annealing.

How small is small? - FEBID and Spatial resolution

FEBID provides a methodology for building sub-10nm structures. Indeed, FEBID has produced some of the smallest synthesized structures in modern technology with spatial resolutions of <3 to 5 nm (see below).



5 and 3nm lines and spaces written on silicon using FEBID from the precursor $MeCpPtMe_3$.

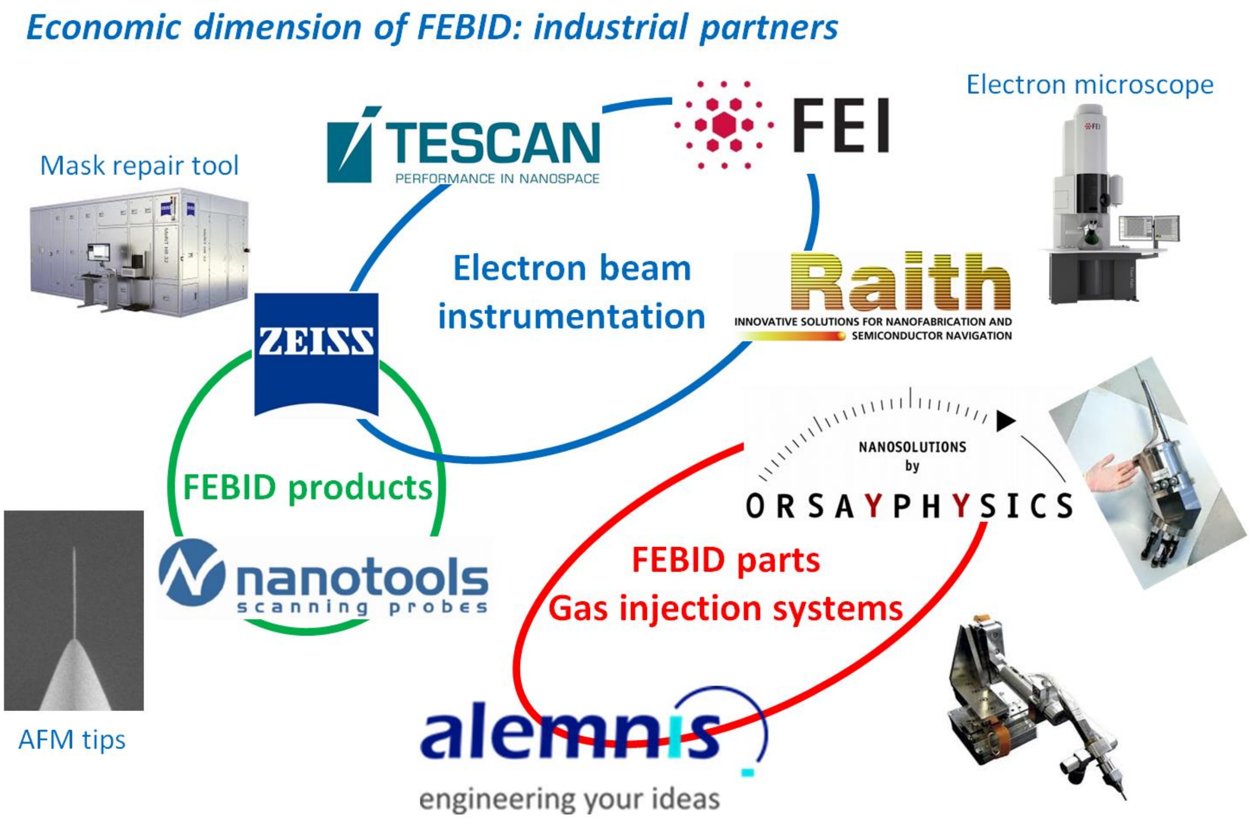
The main limitation in the size of the structures is not only the size of the incident electron beam but the effects of secondary species and diffusion of produced fragments across the substrate surface. Thus fabricated structures are inherently larger than the focused electron beam that produces them. Only by understanding such surface processes can we refine FEBID as a nanotechnology tool and ultimately produce sub-nm architectures. By developing co-operations between surface scientists and FEBID engineers CELINA is pioneering next generation FEBID as a commercially viable nanofabrication technology.

CELINA image and map of the world prepared by FEBID on silicon wafers.

CELINA - Working with Industry

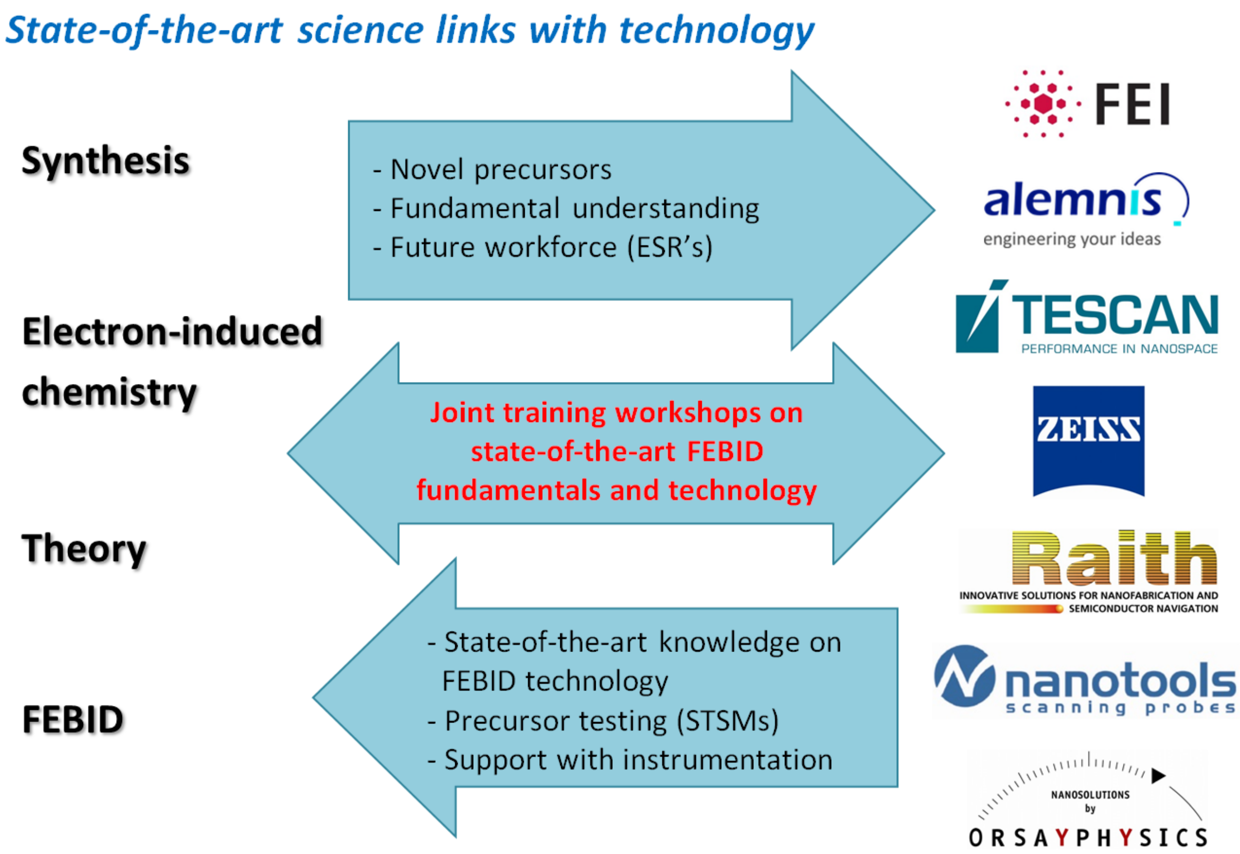
CELINA aims to translate academic knowledge to the industrial community in order to develop FEBID as a commercially viable tool for the fabrication of nanostructures. Research on improved electron beams (higher spatial resolution), new precursors, and their injection systems will lead to improved FEBID products.

A core objective of CELINA is to bring together research in academia with FEBID industry. During the action several new FEBID precursors have been proposed, synthesized and their properties tested in both academic FEBID simulation facilites and in commercial FEBID reactors.



How European industry is developing the techniques for FEBID processing.

CELINA - Bringing academia and industry together



CELINA supports knowledge transfer between European research and FEBID industry.

CELINA has, through its workshops, conferences and the funding of staff exchanges, developed many new research collaborations between academic and Industrial partners. From these collaborations several reviews of the current status of FEBID technology have been prepared. These reviews will be invaluable in producing a 'Roadmap' for development of FEBID over the next decade.

In 2016 a European Training Network, ELENA, has been funded which will bring together leading European FEBID academic and industrial partners to train the next generation of FEBID researchers.

For further details and information on CELINA and FEBID please look at the websites

http://celina.uni-bremen.de/celina/

http://www.cost.eu/COST_Actions/cmst/CM1301

and www.febip.org

or contact the COST Action CELINA Chair

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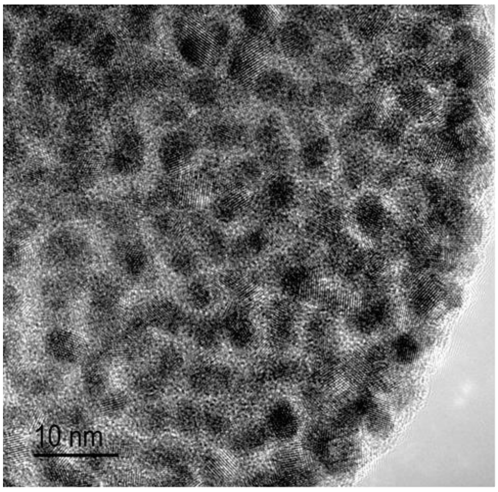

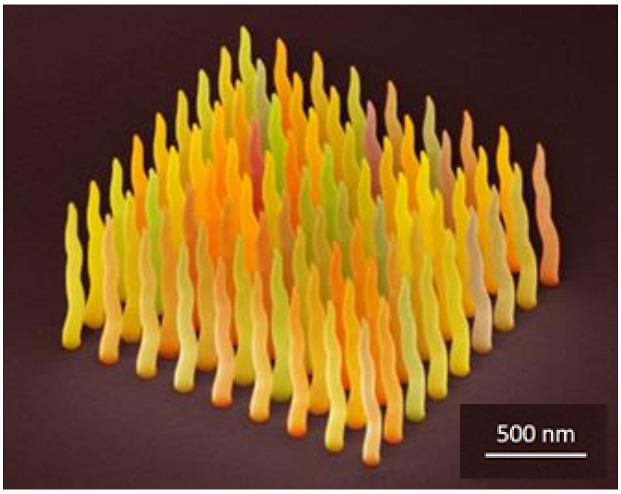

Left; Nanogranular material produced by FEBID and used for gas sensing applications. Right; Nanophotonic array of nanoscale Pt-C pillars (Images from Harald Plank, Graz).

This booklet was assembled by members of CELINA COST Action CM1301