2nd Annual Meeting of COST Action CM 1301, CELINA

Chemistry for ELectron-Induced NAnofabrication

6th – 9th May, 2015, Bratislava, Slovakia

Book of Abstracts

Local Organizer: Peter Papp (Comenius University in Bratislava, Slovakia)

Action Chair: Petra Swiderek (University of Bremen, Germany)

Dear participants of CELINA 2015,

It is our great pleasure to host The 2nd Annual Meeting of COST Action CM1301 – Chemistry for ELectron-Induced NAnofabricatio, in Bratislava, Slovakia between 6th and 9th May 2015. After a successful Kick-off Meeting in Erlangen (March 2014) where we all had a beautiful time we hope that the second meeting will impress you not only by the location in the capital of Slovakia but mostly by its scientific content. At the 2nd Annual Meeting 60 participants will have the opportunity to follow 26 interesting talks given by excellent speakers, 3 invited talks for each Working Group, 7 reports from STSMs in 2014 and 10 Topical lectures requested by the registered participants. Among these high quality lectures 28 interesting posters will be presented on Thursday afternoon by excellent experts in their fields. We hope to fulfil your expectations, not only the scientific but social ones as well, and that conference programme will be at least equally interesting as the 2015 Ice Hockey World Championship held at the same time in the neighbouring Czech Republic.

Let me wish you an interesting meeting here in Bratislava.

Peter Papp

International Scientific Committee of COST Action CM1301 - CELINA

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Local Organizing Committee of The 2nd Annual Meeting of CELINA

Peter Papp	(Comenius University in Bratislava, SK)	Chair
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Michal Lacko	(Comenius University in Bratislava, SK)	
Anita Ribar	(Comenius University in Bratislava, SK)	
Marián Danko	(Comenius University in Bratislava, SK)	

Wednesday, 6th May 2015

13:30 **Registration**

17:50 **Opening** (Congress Hall, 2nd Floor)

Chairman: *P. Swiderek*

18:00 **H. Fairbrother** (Johns Hopkins University, USA) **WG1**
FUNDAMENTAL STUDIES OF ELECTRON INTERACTIONS WITH FEBID PRECURSORS: WHAT WE KNOW, WHAT WE DON’T AND WHAT WE NEED

18:40 **S. Matejcik** (Comenius University, Slovakia) **WG1**
ELECTRON INDUCED DISSOCIATION OF FEBID PRECURSORS

19:10 **Welcome Reception** (Hotel Restaurant, 1st Floor)

Thursday, 7th May 2015

Chairman: *I. Utke*

9:00 **S. F. Rohrlack** (Carl Zeiss SMS GmbH, Germany) **WG3**
PUSHING THE LIMITS OF e-BEAM MASK REPAIR

9:40 **M. Tilset** (University of Oslo, Norway) **WG2**
SYNTHESIS AND CHARACTERIZATION OF GOLD(III) COMPLEXES

10:00 **R. Thorman** (University of Iceland, Iceland) **WG1**
THE ROLE OF LOW-ENERGY ELECTRONS IN FOCUSED ELECTRON BEAM INDUCED DEPOSITION OF RUTHENIUM-CENTERED PRECURSORS

10:20 **Coffee Break** (2nd Floor)

Chairman: O. Ingolfsson

10:40 **A. Ellis** (University of Leicester, UK) **WG1**
ELECTRON-INDUCED CHEMISTRY OF COBALT TRICARBONYL NITROSYL ($CO(CO)_3NO$) IN LIQUID HELIUM NANODROPLETS

11:00 **J. Fedor** (Academy of Sciences of the Czech Republic) **WG1**
EFFECT OF ENVIRONMENT ON ELECTRON ATTACHMENT PROPERTIES: A CASE STUDY OF $C\text{-}C_4F_8O$

11:20 **J. Tamuliene** (Vilnius University, Lithuania) **WG3**
AB INITIO STUDIES OF SILVER PRECURSOR FOR FEBID: Ag(1,1,1,5,5,5 HEXAFLUOROPENTANEDIONATO)(PMe_3) AND $Ag(PMe_3)_2$

11:40 **J. Warneke** (Universität Bremen, Germany) **WG1**
ELECTRON-INDUCED REACTIONS OF ADSORBED AND SOLID CISPLATIN

12:00 **Lunch** (Hotel Restaurant, 1st Floor)

13:30 **Poster Session** (Congress Hall, 2nd Floor)

MC Meeting (Hotel Restaurant, 1st Floor)

15:40 **Coffee Break** (2nd Floor)

Chairman: S. Barth

16:00 **M. Huth** (Goethe University, Germany) **WG3**
FOCUSED ELECTRON BEAM INDUCED DEPOSITION WITH A HETERONUCLEAR PRECURSOR

16:40 **H. Lang** (Chemnitz University of Technology, Germany) **WG2**
GROUP 8 AND 11 TRANSITION METAL COMPLEXES: SYNTHESIS, DECOMPOSITION BEHAVIOR AND THEIR USE IN MOCVD

17:10 **I. Szymanska** (Nicolaus Copernicus University, Poland) **WG2**
APPLICATIONS OF ELECTRON-IMPACT MASS SPECTROMETRY FOR STUDIES OF CARBOXYLATE CHEMICAL VAPOR DEPOSITION PRECURSORS

17:30 **M. Scotuzzi** (Delft University of Technology, Netherlands) **WG3**
NANO PATTERN TRANSFER INTO SILICON AND ITO OF MASKS MADE BY EBID

17:50 **A. Laikhtman** (Holon Institute of Technology, Israel) **WG1**
INTERACTION OF WS_2 NANOPARTICLES WITH IONS AND ELECTRONS STUDIED BY EXPOSURE TO FOCUSED ION AND ELECTRON BEAMS

18:10 **Individual Dinner** (Hotel Sorea, City Center)

Friday, 8th May 2015

Chairman: *M. Allan*

9:00 **A. Devi** (Ruhr University Bochum, Germany) **WG2**

NEW METALORGANIC COMPLEXES FOR TRANSITION METALS: POTENTIAL PRECURSORS FOR FEBID?

9:40 **P. Carsky** (Academy of Sciences of the Czech Republic) **WG1**

PROGRESS IN CALCULATIONS OF CROSS SECTIONS FOR ELASTIC AND VIBRATIONALLY INELASTIC ELECTRON SCATTERING FOR PURPOSES OF CELINA

10:00 **M. Gutowski** (Heriot-Watt University, UK) **WG1**

HYDROGEN RELEASE FROM IRRADIATED AMMONIA-BORANE – A COMPUTATIONAL STUDY

10:20 **Coffee Break** (2nd Floor)

Chairman: *N. Mason*

10:40 **H. Mulders** (FEI Company, Netherlands) **WG1**

CAN EDX BE USED FOR QUANTIFICATION OF HIGH PURITY NANO-SCALE STRUCTURES?

11:00 **L. Amiaud** (Université Paris Sud /ISMO, France) **WG1**

AROMATIC RESIST FILM CHEMICAL TREATMENT USING 50 eV ELECTRONS

11:20 **F. Salvat-Pujol** (Goethe-Universitaet Frankfurt, Germany) **WG3**

SURFACE EXCITATIONS IN ELECTRON-ENERGY-LOSS MODELING FOR FEBID

11:40 **T. Verduin** (Delft University of Technology, Netherlands) **WG3**

ADVANCED SIMULATION OF ELECTRON-SOLID INTERACTIONS

12:00 **Lunch** (Hotel Restaurant, 1st Floor)

13:30 **WG1 Meeting** (Congress Hall, 2nd Floor)

WG2 Meeting (Lounge Hubert, Hotel Lobby)

WG3 Meeting (Hotel Restaurant, 1st Floor)

16:00 **Excursion to the Old Town of Bratislava**

18:00 **Conference Dinner at the Bratislava Castle**

Saturday, 9th May 2015

Early Checkout

Chairman: *J. Kopyra*

9:30 **W. van Dorp** (Technische Universität Dresden, Germany) **WG3**

Au(I) PRECURSORS: VOLATILITY, STABILITY AND RATIONAL DESIGN

10:00 **J. Maljkovic** (University of Belgrade, Serbia) **WG1**

ELECTRON IMPACT DISSOCIATIVE IONIZATION OF TETRAETHYL ORTHOSILICATE

10:20 **Coffee Break** (2nd Floor)

Chairman: *C. W. Hagen*

10:40 **R. Kumar T P** (University of Iceland, Iceland) **WG1**

PRELIMINARY STUDY OF THE EFFECT OF DISSOCIATIVE ELECTRON ATTACHMENT AND DISSOCIATIVE IONIZATION ON THE SPATIAL RESOLUTION IN FEBID

11:00 **A. Bayer** (University of Bielefeld, Germany) **WG1**

HELIUM ION BEAM MILLING: TOWARDS NANOMETER PRECISION

11:20 **S. Hari** (Delft University of Technology, Netherlands) **WG3**

SHAPE–CONTROLLED 3D LITHOGRAPHY BY COMBINED ELECTRON BEAM INDUCED DEPOSITION AND ETCHING

11:40 **Lunch** (Hotel Restaurant, 1st Floor)

Checkout and Departure

Invited Lectures

STSM Reports

Topical Lectures

Fundamental Studies of Electron Interactions with FEBID Precursors: What we know, what we don’t and what we need

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Over the past five or so years there has been a marked increase in studies providing fundamental information on electron interactions with FEBID precursors. In this presentation I will give my personal assessment of the current state of knowledge and research needs, based on these efforts.

What we know:

(i)UHV surface science experiments have shown that the electron-stimulated reactions of the adsorbed precursor during the FEBID process can be broken down into two sequential steps. In the first step, the electron induced deposition of surface bound organometallic precursor’s proceeds through ***desorption*** of one or more of the ligands present in the parent compound. In situations where there are different types of ligands attached to the central metal atom, certain ligands (e.g. CO) appear to be “preferred” leaving groups. Following the initial deposition step, however, subsequent electron-stimulated reactions of the remaining ligands typically lead to ligand ***decomposition*** and it is this second step that is responsible for most of the organic contamination in EBID nanostructures. For example, in the case of metal carbonyls this leads to the overall sequence of reactions:

$$M(CO)_{x(ads)} + e^- \rightarrow M(CO)_{x-y(ads)} + yCO\uparrow_{(g)}$$ – deposition step (CO desorption) – Step 1

$$M(CO)_{x-y(ads)} + e^- \rightarrow MO_{(ads)} + C_{(ads)}$$ – decomposition of residual CO ligands – Step 2

One notable exception to the ligand decomposition step involves metal-halogen bonds which are susceptible to electron-stimulated halide ion desorption,

$$M\text{-}Z_{(ads)} + e^- \rightarrow M_{(ads)} + Z^-_{(g)}$$ (Z = halogen; F, Br, Cl)

Thus, halogen atoms directly attached to the central metal atom in organometallic complexes can be scrubbed by electron processing. This type of information can form the basis of design rules for FEBID precursors. For example, precursors that contain only metal-CO and metal-halogen bonds could produce nanostructures with significantly greater metal content than is current available from existing CVD precursors, possibly even pure metal deposits (e.g. Au(CO)Cl).

(ii) For some precursors where comparisons have been made between results from surface science studies and electron induced reactions of the same precursor molecules in the gas phase (e.g. $MeCpPtMe_3$ and $Pt(PF_3)_4$) the initial deposition step has been shown to proceed via dissociative electron attachment (DEA). For other precursors (e.g. $Co(CO)_3NO$) experimental evidence suggests that both DEA and DI processes may be contributing.

What we don’t know:

(i) Our current theoretical understanding of the FEBID process remains weak. There is no a priori way to predict which ligands will leave in the initial deposition step and how and why the surface bound species formed in the initial deposition step will behave. Similarly, no theoretical studies are available to compare with gas phase measurements on absolute reaction cross-sections and product partitioning as a function of incident energy.

(ii) Fundamental information is lacking on the effect that contaminant gases, diffusion effects and local concentration gradients play in determining reaction probabilities and pathways.

What we need:

(i) Close collaborations with synthetic chemists who can design precursors to test specific hypotheses with the ultimate goal of creating precursors specifically for EBID. This need is being addressed through the inclusion of organometallic chemists

(ii) Studies on how incident electron energies < 100eV impact film composition. This data would provide a means not only to test existing hypotheses about reaction pathways (e.g. DEA vs. DI) but could also serve as a means to tailor the composition of EBID nanostructures.

(iii) Improved interactions between researchers focused on providing fundamental information and those researchers interested in modeling and simulating EBID.

(iv) Fundamental studies on more complex, hetero and polynuclear organometallics.

Acknowledgements: Oddur Ingolfsson (U Iceland), Lisa McElwee-White (U Florida), CELINA, Petroleum Research Fund.

Electron induced dissociation of FEBID precursors

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Dissociative processes induced by low energy electrons to molecules play an important role in different media, such as electric discharges, low and high temperature plasma, atmospheric chemistry, radiation chemistry and as well in the field of Focused Electron Beam Induced Deposition (FEBID). In this paper we are going to present an overview of the research activities as well as the newest results in the field of dissociative processes induced by electrons to FEBID precursors at Comenius University using different experimental techniques (dissociative electron attachment [1,2], dissociative ionization [3-6] and dissociative excitation [7]) and supporting quantum chemical calculations.

We acknowledge support by Slovak research and development agency project APVV-0733-11, VEGA 1/0417/15 and by the COST CMST action CM1301 CELINA.

[1] S. Engmann, M. Stano, Š. Matejčík, and O. Ingolfsson, *Angew. Chem. Int. Ed*., **50 (**2011**)** 9475 –9477

[2] K. Wnorowski, M. Stano, C. Matiaset al., *Rapid Commun. Mass Spectrom.*, **26** (2012) 2093–2098

[3] S. Engmann, M. Stano, P. Papp, et al., *J. Chem. Phys.* **138** (2013) 044305-1-6

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[5] K. Wnorowski, M. Stano, W. Barszczewska et al., *Int. J. Mass Spectr.*, **314** (2012) 42-48

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[7] A. Ribar, M. Danko, J. Országh, et al., Eur. Phys. J. D (2015) in print

Pushing the Limits of e-Beam Mask Repair

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Following the path of Moore's law, complexity of integrated circuits doubles every two years. Therefore demands on photomask technology increase. Challenges and limitation in e-beam induced repair will be presented and also some state-of-the-art techniques to push those limitations regarding minimum feature size.

Synthesis and Characterization of Gold Complexes

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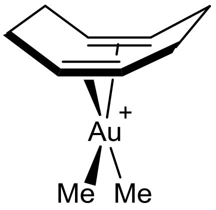
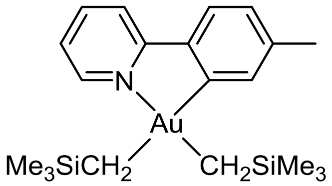
Gold chemistry has become main-stream and is intensely investigated for applications in catalysis, materials science, and much more [1,2]. In general, gold(I) species have attracted most attention with respect to catalysis and other applications due to their ease of synthesis.

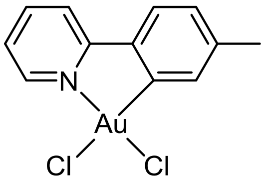
In this contribution, results from our recent ventures into the preparative, structural, and mechanistic aspects of the organometallic chemistry of gold(III) will be presented [3-5]. This will include neutral and cationic complexes, some of which are depicted below. Recent results from in-house ALD experiments will also be presented.



$(cod)AuMe_2^+$



$(tpy)Au(CH_2SiMe_3)_2$



$(tpy)AuCl_2$

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[2] H. Schmidbaur, A. Schier, *Arab. J. Sci. Eng.* **37**, (2012), 1187-1225.

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[5] E. Langseth, A. Nova, E. Tråseth, F. Rise, S. Øien, R. H. Heyn, M. Tilset, *J. Am. Chem. Soc.* **136**, (2014), 10104-10115.

The role of low-energy electrons in focused electron beam induced deposition of ruthenium-centered precursors

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In focused electron beam induced deposition (FEBID), a focused high energy electron beam is used to create three-dimensional structures in the low nm size range. This is achieved by electron-induced decomposition of (often organometallic) precursor molecules at or close to the substrate surface. Due to the impact of the primary electron beam, abundant low energy electrons (LEEs) are emitted from the substrate and deposit surfaces,[1] both inside and outside the radius of the incident electron beam.[2] Two important candidate channels for LEE-induced molecular dissociation in FEBID are dissociative electron attachment (DEA) and dissociative ionization (DI). These likely contribute to adverse effects limiting FEBID, such as deposit broadening and co-deposition of ligands and ligand fragments. The goal of this project is to perform a systematic study on the role of LEEs in precursor dissociation in both the gas and condensed phases, thus distinguishing the dominant processes for different molecular classes.

This talk will discuss the results of a recent STSM on FEBID of the organometallic π-allyl ruthenium tricarbonyl bromide in the context of recent DEA, DI, and surface studies, and a comparison with FEBID of a similar ruthenium-centered metal carbonyl, triruthenium dodecacarbonyl. Ultimately, a suite of gas phase, surface, and in-situ FEBID studies will be performed on this molecule, as well as several other organometallic and metal carbonyl species, in order to elucidate the role of different low-energy electron induced processes in the FEBID nanofabrication process.

Acknowledgements: This work is supported by the Icelandic Research Fund (RANNÍS) and the University of Iceland Research Fund. This work was conducted within the framework of the COST Action CM1301 (CELINA) and RT acknowledges a STSM support from CELINA..

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

Electron-induced chemistry of cobalt tricarbonyl nitrosyl ($Co(CO)_3NO$) in liquid helium nanodroplets

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Co(CO_3NO is the preferred source of Co in FEBID. Deposition of Co allows the writing of thin and precise ferromagnetic films. Potential problems with FEBID as a source of metallic deposits include the loss of writing resolution and the introduction of non-metallic deposits and it is suggested that these may be the result of dissociative electron attachment (DEA) induced by backscattered electrons and secondary electrons. It is therefore important to understand how such processes might occur. Engmann et al. have already investigated the DEA of monomeric $Co(CO)_3NO$ [1]. Here we investigate the DEA processes in superfluid helium nanodroplets. The benefits of using helium nanodroplets include: (1) the ability to rapidly quench reaction products, potentially allowing the identification of unstable reaction intermediates; (2) an exploration of the behavior of $[Co(CO_3NO]_N$ clusters, which should provide a more realistic model of actual FEBID behaviour, which will likely involve thin films of the precursor; (3) the opportunity to add a model substrate, such as a fullerene, to see the effect on the DEA chemistry.

The DEA behavior of both the monomer and clusters are reported here. There are major differences in ion yield curves as a function of electron energy for the clusters relative to the monomer. In addition, the loss of NO is a more prominent channel in helium droplets, indicating that Co-N bonds are unable to form in this environment. Preliminary data will also be presented on the DEA of $Co(CO)_3NO$ on C_{60}.

This work was supported by an STSM (to AME) under CELINA COST Action CM1301.

[1] S. Engmann, M. Stano, Š. Matejčik, O. Ingólfsson, *Angew. Chem. Int. Ed.* **50**, 2011, 9475-9477

Effect of environment on electron attachment properties: a case study of c-C_4F_8O

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In this contribution we address the question how the environment – namely the pressure and the closely related collisional frequency – influences electron attachment properties of c-C_4F_8O. This gas has been chosen due to its high technological potential: it is considered for use as a radiating medium in Cherenkov detectors, as a cleaning agent for CVD chambers or as an SF_6 replacement in high voltage insulation. We determine its attachment cross sections using two complementary setups: (i) an electron-beam experiment equipped with a time-of-flight mass analyzer and (ii) pulsed swarm experiment that uses low concentrations of c-C_4F_8O in various buffer gases. The attachment cross sections in the two experiments are more than one order of magnitude different [1].

The explanation of this extreme difference is based on the properties of the transient negative ion $(C_4F_8O^-)^*$. A certain fraction of these anions survives long enough to be detected even at single-collision conditions of the beam experiment (microseconds). This long lifetime leads to efficient collisional stabilization of anions in the swarm experiment where the collisional frequency is approximately five orders of magnitude larger. Such collisional stabilization (three-body attachment) causes effective attachment rate which is much higher than the one correspoding to the beam cross sections. We argue that a convenient cross section scaling that would describe attachment properties at various pressures is basically impossible due to dependence of the stabilization rate on the buffer gas.

This work has been supported by Project No. 15-12386S of the Czech Science Foundation. The collaboration with the group of prof. C.M. Franck, ETH Zurich is gratefully acknowledged.

[1] A. Chachereau, J. Fedor, R. Janečková, J. Kočišek, M. Rabie, C.M. Franck, *J. Phys. D.: Appl. Phys.*, under review.

Ab initio studies of silver precursor for FEBID: Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe3) and Ag(PMe3)$_2$

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Currently, Focused Electron Beam Induced Deposition (FEBID), allows the structures to be deposited on the nanometer scale, is a very promising technique for nanofabrication. FEBID is an emerging chemical vapor deposition method, which enables resist-free “direct-write” additive nanomanufacturing using a variety of materials with a high degree of spatial and time-domain control. However, this new technology relies on precursors that are not optimized for the electron driven process, therefore the aim of our study is to show that Ag (1,1,1,5,5,5 hexafluoropentanedionato) (PMe3) and Ag (PMe3)$_2$ could be used as precursors of FEBID. The Ag (1,1,1,5,5,5 hexafluoropentanedionato)(PMe3) molecule is stable in to air, moisture and light, does not undergo thermolysis with loss of ligand at temperature below 100 C. The synthesis and handling of the compound is quite simple, and it exhibits the good volatility and absence of thermolysis prior to sublimation, and could form pure-silver-films by thermal chemical vapor deposition [1]. Meanwhile, Ag(PMe3)$_2$ is modeled to show that the molecule could be synthesized and satisfied the known requirements of the precursor of FEBID, too.

In this sense, the thermal and chemical stabilities, toxicity, electronic structure and energy of appearance of the Ag derivatives were investigated. A theoretical method is used to predict all possible fragmentation channels and other processes that could occur under the electron impact on the molecules.

Referring to results obtained, we may conclude that Ag(1,1,1,5,5,5 hexafluoropentanedionato) (PMe3) and Ag(PMe3)$_2$ could be used as the Ag precursor for FEBID.

[1] N. H. Dryden, J. J. Vittal, R. J. Puddephatt', *Chem. Mater*. **VOL**. 5 (1993), PAGES 765-766

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Electron-induced reactions of adsorbed and solid cisplatin

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Unsaturated hydrocarbons, when exposed to low-energy electrons in the presence of NH_3, are efficiently reduced to saturated compounds [1,2]. This led to the idea that the reducing agent NH_3, incorporated as ligand in FEBID precursors, may also have a favourable effect on the removal of the ligands and the release of the pure metal under electron exposure. Although volatile precursors with NH_3 ligands are rare so far, at least cis-diammine-dichloroplatinum(II) (cisplatin) acquires a sufficient vapour pressure when heated. It is thus possible to produce a molecular beam of cisplatin. This has been exploited for a study on dissociative electron attachment to this compound [3] and can also serve to deposit adsorbed layers for studies on its electron-induced decomposition. Motivated by this we have used cisplatin as a model in a proof-of-principle study on the potential advantages of NH_3 ligands in FEBID precursors.

This contribution presents results on the decomposition obtained in a collaborative effort. Experiments using high-resolution electron energy loss spectroscopy (HREELS) of thin adsorbed layers performed in Bremen which reveal the loss of ligands from the adsorbed layers. Scanning electron microscopy of small cisplatin crystals performed in Groningen show a literal ‘boiling’ of the material under the electron beam. Subsequent EDX confirmed a reduction to clean platinum. In contrast, deposits produced in a FEBID machine at EMPA, Thun, using a high temperature evaporation source operating at 200°C, retained a significant amount of chlorine. Possible reasons for these contrasting results will be discussed.

JW acknowledges support through an STSM grant under COST Action CM1301 (CELINA).

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Focused electron beam induced deposition with a heteronuclear precursor

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Focused electron beam induced deposition (FEBID) has proven to be an extremely flexible direct-write method for the fabrication of magnetic nanostructures. With careful optimization of the preparation conditions largely carbon- and oxygen free deposits of Co and Fe can be obtained from the carbonyl based precursors $Co_2(CO)_8$ and $Fe(CO)_5$, respectively [1,2]. Recently, it was shown that Co deposits can be further purified by an in-situ post-growth treatment in H_2 at elevated temperatures and under electron irradiation [3]. From the point of view of using FEBID structures for micromagnetic studies one would like to advance in several directions: (1) multi-component (binary, ternary) magnetic FEBID structures with, e.g., tunable magnetic properties; (2) alternative precursors which are reasonably easy to handle in the FEBID process and result in deposits with high metal content. Regarding the first point, in recent work two precursors have been used in parallel resulting in either the dilution of the magnetic phase [4] or the formation of a hard magnetic alloy [5]. However, in these cases the obtained material contained a significant volume fraction of the carbonaceous matrix. Here we present first results on the use of the heteronuclear precursor $HFeCo_3(CO)_{12}$ (see inset in figure) in FEBID that directly results in the formation of a ferromagnetic alloy phase with a metal content up to 80 at% [6]. First measurements of the temperature-dependent resistivity reveal metallic behavior with a tendency for localization below 50 K (see main figure). This likely places the as-grown material on the metallic side close to a metal-insulator transition.

This work was conducted within the framework of the COST Action CM1301 (CELINA).

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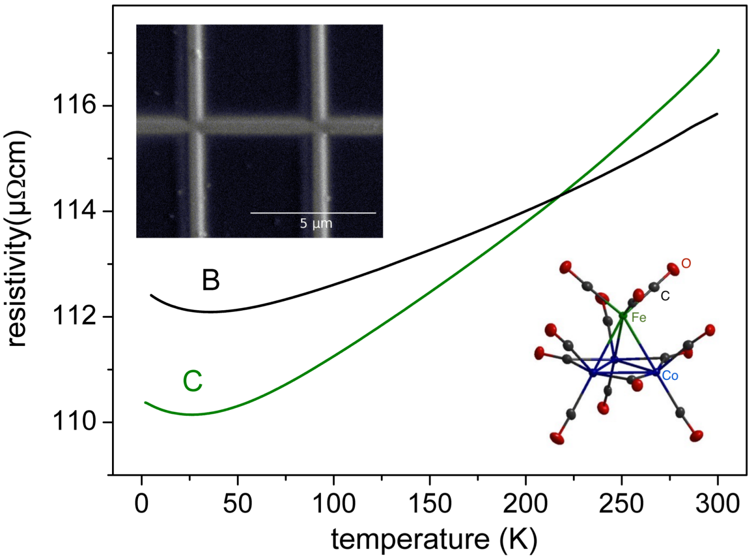

Temperature-dependent resistivity of $Fe_{1-x}Co_xC_yO_z$ FEBID structures. Sample B: as grown. Sample C: subjected to post-growth electron irradiation. Inset upper left: SEM image of six-probe structure used for the transport measurement. Inset lower right: precursor structure (hydrogen not shown).

Group 8 and 11 Transition Metal Complexes: Synthesis, Decomposition Behavior and their Use in MOCVD

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

One of our group topics deals with the specific design of novel, volatile MOCVD precursors for conductive, semi-conductive and magnetic layer formation. We herein present an approach for precursor design and their systematic use as CVD precursors for thin metal layer formation on the example of Cu, Ag and Ru layer growth. For pure Cu and Ag layer formation the use of the metal-organic complexes $[M(O_2CR')(PR_3)_n]$ and $[M(\beta\text{-diketonate})(PR_3)_m]$ (M = Cu, Ag; R, R' = organic ligand; β-diketonate = acac, hfac, … ; n = 0, 1, 2, 3; m = 1, 2) as CVD precursors will be described. [2] The organic groups R and R' in coherence with the number n or m of the coordinated Lewis-base ligands PR_3 do have a great influence on the decomposition parameters and hence on the layer formation process, which also will be highlighted. This strategy will also be explained by using Ru-carboxylates, Ru-β-diketonates and Ru-(half)sandwich compounds as suitable MOCVD precursors for the generation of pure and conformal thin Ru layers. [3]

The decomposition mechanism for the above mentioned species will be discussed as well.

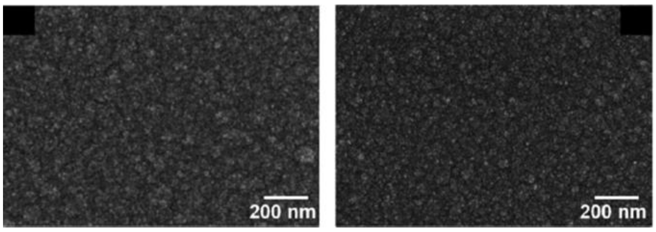

Fig. 1: SEM images of Ru films generated from $[Ru(\eta^5\text{-}C_5H_3{}^tBuSiMe_3)(\eta^5\text{-}C_5H_4{}^tBu)]$ (left) and $[Ru(\eta^5\text{-}C_5H_3{}^tBuSiMe_3)_2]$ (right). [3]

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Applications of Electron-Impact Mass Spectrometry for Studies of Carboxylate Chemical Vapor Deposition Precursors

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Copper, silver and palladium carboxylate compounds can be applied as precursors in a Chemical Vapor Deposition process for a metallic nanolayers formation. Copper and silver exhibit high electrical and thermal conductivity; therefore they are extensively used in microelectronics. Moreover, bimetallic composites Cu/Ag can be alternative materials, used as interconnects. Palladium is an important component in catalytic systems. Titanium carboxylate-alkoxides are able to be applied for the titanium dioxide thin films deposition. This oxide is an important material due to its optical and electrical properties, chemical stability, and low cost. Doping titanium dioxide with transition metals *e.g.* copper leads to improvement of its optical properties (*e.g.* photocatalytic activity).

In the case of single precursors electron-impact mass spectrometry was used for the metal carriers type, structure and stability studies in the gaseous phase. The influence of carbon chain length in perfluorinated carboxylate ligands ($R = C_nF_{2n+1}$, n=1-9) and the kind of secondary ligand in the complexes (*e.g.* $CH_2{=}C(H)SiR'_3$, $(CH_2{=}CHCH_2)_2SiMe_2$, $R'NH_2$) were discussed. Moreover, the fragmentation schemes for each group of compounds were proposed [1,2].

Furthermore, systems of silver/copper compounds and copper/titanium dioxide precursors were studied by EI-MS. The precursor mixture composition influence on the type of obtained materials was studied. The products of ligand or metal exchange reactions can be observed [3].

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Nano pattern transfer into Silicon and ITO of masks made by EBID

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Resist-based electron beam lithography does not routinely provide sub-10 nm resolution. The project Single Nanometer Manufacturing for beyond CMOS devices (SNM) [1] aims at achieving that, using Nano Imprint Lithography (NIL). NIL stamps can be fabricated using mask patterns made by Electron Beam Induced Deposition (EBID), and transfer them into the stamp material. We studied the pattern transfer into Silicon of sub-10 nm masks, with $MeCpPtMe_3$ as an EBID precursor, and different plasma etching recipes using HBr, Chlorine- or Fluorine-based chemistries. A typical mask consists of arrays of dots and sets of lines with width down to 8 nm and height of 0.5 nm. These patterns were successfully transferred into Si using SF_6/C_4F_8 chemistry, resulting in a height ratio of 8 and a width of 9.8nm, as shown in Fig.1. However, Step and Flash Nano Imprint Lithography (SFIL) requires UV transparent stamps [2]. We used glass substrates covered with ITO, that serves as a conductive layer. The EBID masks, made using the same Platinum precursor, consist of a set of 10 lines. The pattern transfer was carried out using $CH_4/H_2/Ar$ chemistry, that is known to etch ITO [3]. Fig. 2 shows a SEM micrograph of the etched mask. The resulting height ratio was measured to be 1.5. Etching with BCl_3/Cl_2 chemistry provided a somewhat larger selectivity of about 2. We will present more detailed results on the various processes we used.

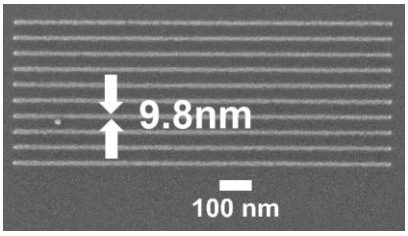

Fig. 1: SEM image of the EBID mask on Si after etching (SF_6/C_4F_8)

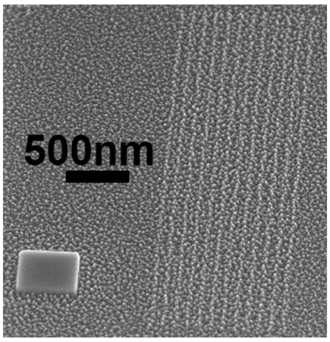

Fig. 2: SEM image of the EBID mask on ITO after etching ($CH_4/H_2/Ar$)

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Interaction of WS_2 Nanoparticles with Ions and Electrons Studied by Exposure to Focused Ion and Electron Beams

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The effect of FEB and FIB on the structure of fullerene-like (IF) nanoparticles (NP) of WS_2 was studied to simulate the conditions in RF and microwave hydrogen/deuterium plasma. IF-WS_2 NP were exposed to D_2 plasma, to investigate their capability to serve as a media for hydrogen storage. The concentrations of the absorbed deuterium in the NP were in the range of 0.4-1.5 wt. %. The micro-Raman measurements confirmed that this deuterium is in the form of D_2.

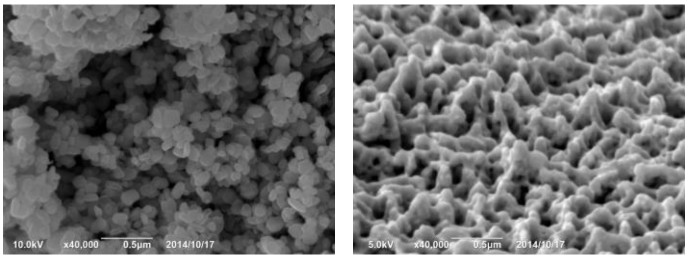

Figure1. SEM images of the IF-WS_2 NP before (left image) and after (right image) bombardment by FIB.

To investigate the effect of ions and electrons on IF-WS_2, they were exposed to FEB and FIB of Ga^+ ions. FEB bombardment resulted in some contamination due to the environment with no substantial modification of the NP structure. IF-WS_2 NP were bombarded by the FIB of Ga^+ at various doses. Using EDS, we detected some minor implantation of Ga along with negligible changes in the content of residual oxygen and carbon. The primary effect of FIB was the drastic change of the near surface structure and morphology of the bombarded region. From Fig. 1, melting or sublimation with subsequent recrystallization of the NP took place. This was confirmed by the micro-Raman which showed degradation of the crystalline perfection by decrease in the intensities of the characteristic peaks of WS_2. However, no contamination, oxidation, or decomposition of the IF-WS_2 was detected after FIB treatments. These results can explain why physisorbed (intercalated) D_2 is stable at the room temperature in the plasma - treated IF-WS_2, indicating that such "melting" could take place then resulting in closing some of the pores through which hydrogen/deuterium atoms diffuse inside these layered NP.

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New metalorganic complexes for transition metals: Potential precursors for FEBID?

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The transformation of molecules to materials in the form of nanostructures has been well established employing vapour phase deposition processes such as metalorganic chemical vapour deposition (MOCVD) and atomic layer deposition (ALD). The underlying precursor chemistry is one of the main parameters that dictate these processes and there has been steady progress made in terms of precursor design and development that suits the demands of advanced technologies. Recently there has been a tremendous surge in research activities in the field of focused electron beam induced deposition (FEBID), a technique projected to have a great potential for future technological applications. In this case too, the precursors have to possess certain requirements to fabricate the nanostructured materials especially with the right composition/stoichiometry and microstructure. The volatility and stability of the precursors are of prime importance. The question that is often asked is, can CVD or ALD precursors be directly adapted for FEBID applications?. How can one tune the precursor properties making them more conducive for FEBID?. Going away from the classical precursors is a high risk. On the other hand, there is certainly scope in tuning the physico-chemical properties of metalorganic precursors rendering them suitable for FEBID. In this presentation, the new developments in terms of precursor chemistry of selected transition metals particularly meant for CVD/ALD will be presented. The comparison will be made using ligands where the transition metal is surrounded by either all-nitrogen or mixed-oxygen nitrogen coordinated ligands. Can we envisage some potential of these new metalorganic precursors in FEBID as well?.

Acknowledgement: This presentation is supported by the COST Action CM1301(CELINA) and is gratefully acknowledged.

Progress in calculations of cross sections for elastic and vibrationally inelastic electron scattering for purposes of CELINA

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Recently [1,2] we have succeeded to improve considerably our theoretical model and our program. Now it can be applied to larger molecular systems than it was possible so far. The program retains still its rigor of a true theoretical "ab initio" model, and hence, it provides reliable predictions for elastic and vibrationally inelastic electron scattering. We will show how our calculations were helpful for interpretation of experimental results of Michal Allan for diacetylene and cyclopropane. A few examples will show comparison of experimental and theoretical EEL spectra, comparison of energy and angular dependences of cross sections, and interpretation of observed resonances.

Next we plan treatments of molecules considerably larger than diacetylene and cyclopropane. For keeping our project on track useful for CELINA, we take this opportunity for asking the WG1 and WG3 participants the following questions:

1. We are ready to work on a model for a precursor adsorbed on a solid. What a precursor and solid it should be ?
2. From calculated energy dependences we can find and interpret resonances in detail. Can such predictions be of any use?
3. We can provide a detailed insight in vibrational excitation by electron impact. Is it of any use?
4. We believe we can estimate how deep can low-energy electrons penetrate into a solid. Is such an information relevant for FEBID ?

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Hydrogen Release from Irradiated Ammonia-Borane – A Computational Study

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We modelled the effect of ionization on hydrogen release pathways in ammonia borane, NH_3BH_3, (AB). The cation of AB is first-order Jahn-Teller unstable and the C_{3v} structure of the neutral deforms to a C_s symmetry structure with two BH bonds elongated by 0.05 Å and the H-H distance reduced to 1.19 Å. The three equivalent C_s symmetry minima ($^2A''$) are separated by C_s symmetry transition states ($^2A'$) and the barrier for pseudorotation is 15 kJ mol^{-1}. The dissociation of AB^+ into NH_3 and BH_3^+ requires 353 kJ mol^{-1}. Thus the BN bond is strengthened in the cation by ca. 250 kJ mol^{-1} in comparison with the neutral AB. The ionization of BH_3 to BH_3^+ increases its Lewis acidity and strengthens the dative bond with the Lewis base NH_3. The release of a hydrogen atom from AB^+ requires only78 kJ mol^{-1}. AB^+ is prearranged for H_2 release due to the Jahn-Teller distortion and the barrier is 96 kJ mol^{-1}. The product NH_3BH^+ isomerizes to $NH_2BH_2^+$ with a barrier of 138 kJ mol^{-1}. Reaction pathways for the release of hydrogen from the clusters of AB involving ionized and/or partially dehydrogenated NBH_m^+ species will be discussed.

Can EDX be used for quantification of high purity nano-scale structures?

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EDX is a commonly applied technique to determine the elemental composition of a material exposed to electron irradiation. This technique is originally referred to as micro-analysis. In many FEBIP related research the technique is also used to monitor the material quality of the deposited materials. In this case however, the basic requirements for EDX are not fulfilled and hence the answers are wrong or at least very misleading. Especially the low Z elements such as C and O are very sensitive to effects such as self-absorption and geometric constraints, especially in a high Z environment such as Pt or Au. Issues related with this technique will be addressed and the limits of the applicability will be discussed. EDX is certainly very valuable, but application outside its regular boundary conditions has to be done with great care and understanding of the underlying phenomena.

Aromatic resist film chemical treatment using 50 eV electrons

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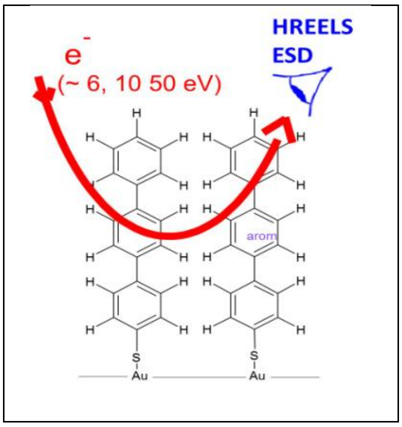
Low energy electron (LEE, energy ≤ 50 eV) induced fragmentation is a widespread mechanism of surface molecular modification. An example of local transformation induced by electron impact is the cross-linking in aromatic SAMs. Cross-linked SAMs exhibit an improved stability, a high etching resistance, block electrochemical deposition and can be chemically functionalized [1]. Aromatic self-assembled monolayers (SAMs) have been proposed as platforms for development of carbon nano-membranes and can be used as resist film for lithography [2].



In order to have a better control of induced transformation in aromatic resist films, we have studied model aromatic SAMs of 1,1',4',1"-Terphenyl-4-thiol on gold [3,4]. High Resolution Electron Energy Loss Spectroscopy (HREELS) and Electron Stimulated Desorption (ESD) of neutral fragments measurements were combined. Considering that the fragmentation processes and the nature of released fragment are strongly dependent on electron incident energy in the low energy range [5], chemical transformations induced by electron irradiation for incident energies of 6, 10 and 50 eV will be compared. Special attention will be given to the change of hybridization state of the carbon centres and to possible partial layer etching.

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Surface Excitations in Electron-Energy-Loss Modeling for FEBID

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Surface excitations are typically not accounted for in the modeling of electron energy losses for focussed-electron-beam-indeuced deposition (FEBID) experiments [1-2]. These excitations are, on the one hand, responsible for a sizable fraction of the intensity in electron-energy-loss spectra for electron energies of up to 1-2 keV and, on the other hand, they constitute an essential ingredient for low-energy-electron transport through surfaces, in particular for secondary-electron emission processes.

Recent electron-coincidence measurements, which have been able to elucidate the role played by surface excitations in secondary-electron emission, will be presented [3], accompanied by a description of surface energy losses within the semiclassical dielectric formalism which was instrumental in interpreting the experimental data [4]. Relevant aspects for the modeling of electron transport in FEBID experiments will be highlighted.

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Advanced dynamic simulation of electron-solid interactions

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A simulation of the growth of a deposit using Focused Electron Beam Induced Processing (FEBIP) typically includes an electron beam, substrate and a precursor gas. One of the key elements in FEBIP simulations is the electron-solid interaction. In literature, we have found that most Monte-Carlo simulations are based on Rutherford cross-sections and the fast-secondary electron model of Joy[1-3]. However, more sophisticated physical models for inelastic scattering have been developed and employed[4-7]. Unfortunately, to our best knowledge, these models are not typically used in the FEBIP community.

Recently, we have developed a program for electron-solid interactions for the purpose of SEM imaging and lithography simulations[8]. The inelastic scattering is based on dielectric function theory[4-6] and includes refinements for low-voltage applications as given by Kieft and Bosch[6]. The elastic scattering in our program is also different from what is typically used in FEBIP simulations. Instead of Rutherford cross-sections, we have used the relativistic Mott cross-sections based on the work of Czyzewski et al[9]. In addition, we have added a model for acoustic phonons to account for the scattering of low energy electrons[7]. The main advantage of these more sopisticated models is the accurate predicition of secondary electron yields without the requirement of scaling the result to experimental values.

Our program, with respect to existing simulators using similar models, is special because a geometry is defined in terms of cells and it is the use of atomic-sized cells that enables the simulation of real-time dynamic FEBIP-like processes. Furthermore, the code is optimized for high performance by using hybrid shared memory (OpenMP) and distributed memory (OpenMPI) parallelism. We will present our simulation code and some results to demonstrate its possible use in the FEBIP community.

We thank Kieft and Bosch from FEI company for using their SEM simulator[6], which has been an essential ingredient of this work. Special thanks to Erik Kieft for discussions during the development of our home-built simulator.

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Au(I) precursors: volatility, stability and rational design

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We can turn electron microscopes into a platform for chemical synthesis on the nanometer scale using focused electron beam induced processing (FEBIP). A beam of electrons is focused onto a sample surface, in the presence of a gas. The gas molecules adsorb on the sample and react under the influence of the electrons. The reaction product can be (for instance) a solid residue.

The precursor gases used for deposition typically yield reaction products of poor quality. This is mainly because the precursors are not tuned specifically to electron-induced chemistry. The past few years improved deposition conditions and new methods for post-deposition processing have significantly improved the deposit quality. However, we can develop many more applications for FEBIP and simplify the fabrication process greatly if we can find dedicated FEBIP precursors.

High-purity gold deposition is interesting for many applications, such as plasmonics or the directed self-assembly of functional organic molecules. Au(I) compounds appear to be promising Au precursors. For instance, $ClAu^{I}PF_3$ and $ClAu^{I}CO$ yield pure Au deposits in a single step [1,2]. Unfortunately, both are highly unstable in vacuum and decompose in ~1 hour. On the other hand, $ClAu^{I}PMe_3$ is stable, but is not volatile. And $MeAu^{I}PMe_3$ is stable and volatile, but the PMe_3-ligand is not removed by the electrons, resulting in a carbon-polluted deposit. What is the origin of the short lifetime of $ClAu^{I}CO$ in vacuum? Why is $MeAu^{I}PMe_3$ volatile while $ClAu^{I}PMe_3$ is not? And can we, when we answer these questions, design a better Au precursor?

We study six organometallic Au(I) complexes and combine data from scanning electron microscopy, single crystal x-ray diffraction and density functional theory calculations. The results show a consistent trend, revealing the origin of the stability and volatility or Au(I) complexes. Based on this we come to the first rational design of a dedicated Au precursor for FEBIP.

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Electron impact dissociative ionization of tetraethyl orthosilicate

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We have investigated dissociative electron ionization of tetraethyl orthosilicate, TEOS ($Si(OC_2H_5)_4$), in gas phase, interesting as a possible Focused Electron Beam Induced Dissociation (FEBID) precursor. Measurements were performed at Comenius University on the crossed beams apparatus [1] and the cluster apparatus [2]. Both are equipped with trochoidal electron monohromator, which produces well collimated electron beam crossed perpendicularly with target. Positive ions formed with electron molecular interactions are extracted by a small electric field and recorded by quadrupole mass analyser. We have measured the possible pattern of fragmentation for TEOS molecule and compared with the NIST mass spectrum. Beside parent $M=(Si(OC_2H_5)_4)^+$ at m/z 208 many other positive ions were recorded in the mass spectrum, with many SiO_x^+ fragments (x= 2, 3 and 4) and their hydrogenated alternatives between m/z 60 and 100. Only the loss of 1 or 3 CH_3 or C_2H_5 was typical for TEOS, contrary to the loss of 1 or all 4 OC_2H_5 ligands. Alternative fragmentation paths were the loss of 2 CH_3 + CH_2CH_3; CH_3 + C_2H_5 + OC_2H_5; 2 C_2H_5 + OC_2H_5; CH_3 + 2 C_2H_5 + OC_2H_5. Beside that, measurements of threshold energies for all TEOS fragments have been done.

This work was supported by the Slovak Research and Development Agency under Contract No. APVV-0733-11; the Slovak grant agency VEGA V/0514/12; Ministry of Education and Science of Republic of Serbia (Project No. 171020). This work was conducted within the framework of the COST Action CM1301 (CELINA).

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Preliminary study of the effect of dissociative electron attachment and dissociative ionization on the spatial resolution in FEBID

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In Focused Electron Beam Induced Deposition (FEBID) the lateral extension of the structures created, is generally greater than the diameter of the primary electron beam. This is in part attributed to the effect of secondary electrons (electron energy < 50 eV) emitted from the substrate's surface outside the focal point of primary beam. Fragmentation channels active in the energy range below 50 eV are Dissociative electron attachment (DEA), Dissociative Ionization (DI), Neutral Dissociation (ND) and Dipolar Dissociation (DD). Gas phase experiments have shown that commonly used FEBID precursor molecules may have considerable DEA and DI cross-sections [1, 2]. The effects of these channels on the spatial resolution of FEBID nanostructures, however, are not well understood. In the current work we have studied the lateral broadening of nanostructures and the proximity effect in FEBID using the potential precursor molecules; 1,1-dichloro-1-silacyclohexane (DCSCH), silacyclohexane (SCH) and 1,3,5-trisilacyclohexane (TSCH). In gas phase studies [3] we have shown that DCSCH has fair cross section for DEA as well as DI. On the other hand, SCH is apparently 'inert' towards DEA. For TSCH we expect similar behavior as has been observed for SCH.

In the current study the change in nano-pillars base diameter with increasing electron beam exposure time was measured for DCSCH and TSCH, and the proximity effect was compared between SCH and DCSCH. For TSCH the pillar base diameter was found to saturate much sooner than for DCSCH. Likewise, the proximity effect for DCSCH was more apparent than for SCH. Here we discuss these results in context to the relative DEA and DI cross sections measured for these compounds in the gas phase.

Acknowledgments: This work was supported by Icelandic Centre for Research (RANNIS). R K. T. P acknowledges a STSM support from the COST Action CM1301 (CELINA).

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Helium Ion Beam Milling: Towards Nanometer Precision

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The Helium Ion Microscope (HIM) is a charged particle microscope employing helium ions for probing the sample. In the low dose regime, the HIM operates as microscope, high doses enable material modification and sputtering. Compared to conventional focussed 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 as well as for the inspection of nanostructures. The He^+ beam with its unique properties overcomes the resolution limit of conventional FIB tools as we show in a comparison with a high resolution Ga-FIB. We achieve He^+-milled nanostructures with a smallest feature size of about 3 nm. In particular, we demonstrate He^+-milling of nanopores with such diameters in a number of membrane types: 30 nm thick Silicon Nitride, Graphene and 1 nm thick carbon nanomembranes (CNM) made from aromatic self-assembled monolayers by electron-induced cross-linking. Furthermore, we show He^+-milling of few nanometer-sized gaps in plasmonic nanostructures [1] as well as in carbon nanotubes [2]. Different strategies for the characterization of nanostructrues with the HIM will be discussed. In particular, we compare the feasibility of the ion generated secondary electron signal to the He^+ transmission signal.

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Shape–controlled 3D lithography
by combined Electron Beam Induced Deposition and Etching

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3D shape control is an essential requirement in the development of novel lithography techniques such as Electron Beam Induced Deposition (EBID). While it is in principle a high resolution technique, there is little control over the shape of the lines due to additional processes initiated by secondary and backscattered electrons from the substrate. Therefore, EBID line profiles are typically Gaussian with sloping sidewalls[1]. We present here a technique to fabricate nanopatterns with vertical sidewalls, and therefore well-defined widths, by using a combination of Electron Beam Induced Etching (EBIE) and Deposition[2]. This method has the advantage of being high resolution, resist-free and fully implemented inside the SEM. Carbon structures about 500 nm wide were patterned in an FEI Helios 650 Dual Beam system by EBID on a silicon substrate having a 20 nm gold-palladium layer. Fig. 1(a) shows the FIB cross section of the as-deposited structure covered with a protective platinum layer. EBIE of carbon by water[3] was performed at the two sides of the deposit using $MgSO_4.7H_2O$ as a supply for water molecules in the presence of a 5 keV electron beam. The creation of vertical sidewalls upon etching as shown in the FIB cross section in Fig 1(b) clearly demonstrates the success of this technique. We aim to extend this method to the sub-20 nm regime to etch away the Gaussian sidelobes that typically lead to interconnects in dense EBID lines and spaces. Based on this proof of principle, further experiments were performed and quantitative measures of size and shape control will be presented.

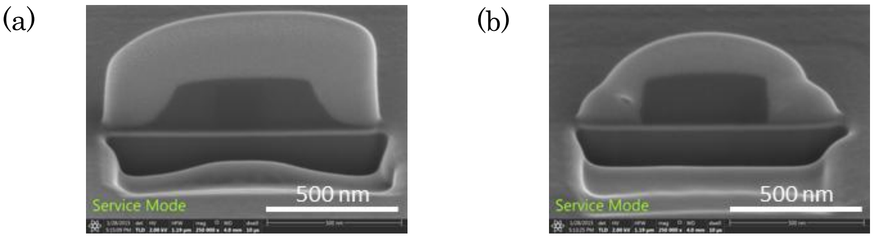

Fig 1 (a) FIB cross section of as-deposited EBID structure and (b) EBID structure after etching, clearly demonstrating the creation of vertical sidewalls.

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Poster Presentations

13:30, Thursday, 7th May 2015

P01 **M. Allan** (Université de Fribourg, Switzerland) **WG1**

ELECTRONS AND IONIC LIQUIDS – A NOVEL APPROACH TO STUDY ELECTRON SCATTERING OF NONVOLATILE COMPOUNDS

P02 **C. Dablemont** (Université Paris Sud / ISMO, France) **WG1**

INTERFACE WETTABILITY PROPERTIES OF 11-MERCAPTOUNDECANOIC ACID SAMS

P03 **R. Thorman** (University of Iceland, Iceland) **WG1**

A SIDE-BY-SIDE COMPARISON OF COMPREHENSIVE GAS PHASE, SURFACE, AND IN-SITU STUDIES OF TWO FEBID PRECURSORS: $MeCpPtMe_3$ AND $\Pi\text{-}C_3H_5Ru(CO)_3Br$

P04 **O. Ingolfsson** (University of Iceland, Iceland) **WG1**

AMPLIFICATION OF ELECTRON ATTACHMENT INDUCED FRAGMENTATION THROUGH NEW BOND FORMATION AS A POSSIBLE ROUT IN PRECURSOR DESIGN. PART I; CO AND F_2CO FORMATION FROM TETRAFLUORO-PARA-BENZOQUINONE.

P05 **O. Ingolfsson** (University of Iceland, Iceland) **WG1**

AMPLIFICATION OF ELECTRON ATTACHMENT INDUCED FRAGMENTATION THROUGH NEW BOND FORMATION AS A POSSIBLE ROUT IN PRECURSOR DESIGN. PART II; HF AND CO FORMATION FROM ORTHO- AND PARA-TETRAFLUOROHYDROQUINONE.

P06 **J. Kopyra** (Siedlce University, Poland) **WG1**

ELECTRON INDUCED REACTIONS IN FLUORINATED ACETAMIDE AND ITS METHYL ESTER

P07 **R. Kumar T P** (University of Iceland, Iceland) **WG1**

GAS PHASE DISSOCIATIVE ELECTRON ATTACHMENT AND DISSOCIATIVE IONIZATION OF 1,1-DICHLORO-1-SILACYCLOHEXANE, SILACYCLOHEXANE AND 1,3,5-TRISILACYCLOHEXANE; COMPARISON OF THE PERFORMANCE OF THESE MOLECULES IN FEBID

P08 **M. Lacko** (Comenius University in Bratislava, Slovakia) **WG1**

ELECTRON INDUCED REACTIONS OF IRON CARBONYL COMPLEXES

P09 **B. Marinkovic** (University of Belgrade, Serbia) **WG1**

ELECTRON IMPACT EXCITATION OF THE BISMUTH RESONANCE LINE

P10 **C. Matias** (University of Innsbruck, Austria) **WG1**

LOW-ENERGY ELECTRON INTERACTIONS WITH TUNGSTEN HEXACHLORIDE

P11 **J. Orszagh** (Comenius University in Bratislava, Slovakia) **WG1**

ELECTRON INDUCED FLUORESCENCE AS A TOOL FOR STUDYING PRECURSOR DISSOCIATION

P12 **K. Regeta** (Ruhr University Bochum, Germany) **WG1**

ABSOLUTE CROSS SECTIONS FOR ELECTRONIC EXCITATION OF PYRIMIDINE

P13 **K. Regeta** (University of Fribourg, Switzerland) **WG1**

TWO-DIMENSIONAL SPECTRA OF ELECTRON COLLISIONS WITH ACRYLONITRILE AND METHACRYLONITRILE REVEAL NUCLEAR DYNAMICS

P14 **A. Ribar** (Comenius University in Bratislava, Slovakia) **WG1**

ELECTRON INDUCED FLUORESCENCE STUDY OF IRON PENTACARBONYL: IRON ATOM LINES

P15 **M. Danko** (Comenius University in Bratislava, Slovakia) **WG1**

ELECTRON INDUCED FLUORESCENCE STUDY OF IRON PENTACARBONYL: CARBONYL BANDS

P16 **F. Vollnhals** (FAU Erlangen-Nürnberg, Germany) **WG1**

ELECTRON BEAM INDUCED SURFACE ACTIVATION AS A MEANS TO STUDY FUNDAMENTAL ASPECTS OF ELECTRON SCATTERING PROCESSES

P17 **F. Vollnhals** (FAU Erlangen-Nürnberg, Germany) **WG1**

FABRICATION OF CARBON-FREE COBALT NANOSTRUCTURES ON PORPHYRIN-COVERED TiO_2(110) USING THE PRECURSOR $Co(CO)_3NO$

P18 **Z. Wang** (Universität Bremen, Germany) **WG1**

NOVEL INSIGHTS INTO THE WATER-ASSISTED PURIFICATION OF FEBID DEPOSITS PRODUCED FROM MeCpPtMe3

P19 **S. Barth** (Vienna University of Technology, Austria) **WG2**

SYNTHESIS AND CHARACTERIZATION OF HETEROMETALLIC CARBONYLS FOR FOCUSED ELECTRON BEAM INDUCED DEPOSITION

P20 **E. Pousaneh** (Chemnitz University of Technology, Germany) **WG2**

SYNTHESIS AND THERMAL BEHAVIOR ANALYSIS OF NEW YTTRIUM BETA-DIKETONATE PRECURSORS FOR INVESTIGATION AS A CHEMICAL VAPOR DEPOSITION

P21 **J. Jeschke** (Technische Universität Chemnitz, Germany) **WG3**

CHEMICAL VAPOR DEPOSITION OF CONFORMAL PHOSPHORUS-DOPED RUTHENIUM LAYERS

P22 **A. Romano-Rodriguez** (Universitat de Barcelona (UB), Spain) **WG3**

PLATINUM PURIFICATION FOR HIGHER CONDUCTIVE CONTACTS OF INDIVIDUAL SnO2 NW GAS SENSOR

P23 **M. Scotuzzi** (Delft University of Technology, Netherlands) **WG3**

SPATIAL RESOLUTION OF EDX FOR THE DETECTION OF NANOSTRUCTURES

P24 **M. Sezen** (Sabanci University, Turkey) **WG3**

GAS ASSISTED ETCHING OF HIGH DENSITY POLYETHYLENE (HDPE) FOR THE DEVELOPMENT OF FUNCTIONAL SURFACES

P25 **M. Moonir Shawrav** (Vienna University of Technology, Austria) **WG3**

IN-SITU CONTROLLED FOCUSED ELECTRON BEAM INDUCED ETCHING OF SEMICONDUCTOR NANOWIRES

P26 **P. Taus** (Vienna University of Technology, Austria) **WG3**

PURIFICATION OF ELECTRON BEAM INDUCED DEPOSITED GOLD NANOSTRUCTURES

P27 **F. Venturi** (University of Modena and Reggio Emilia, Italy) **WG3**

MFM AND TEM ANALYSIS OF Co SQUARE MAGNETIC RINGS

P28 **H. D. Wanzenboeck** (Vienna University of Technology, Austria) **WG3**

FEBID OF Fe AND Co NANOPILLARS - A VERSATILE APPROACH FOR HIGH ASPECT RATIO AND LOW MOMENTUM MAGNETIC TIPS FOR MAGNETIC FORCE MICROSCOPY

Electrons and ionic liquids – a novel approach to study electron scattering of nonvolatile compounds

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We have applied the technique of low-energy electron impact spectroscopy to ionic liquids (ILs) suspended on a loop of molybdenum wire in a spectrometer normally used for gas phase studies.

Figure 1. The IL droplet.

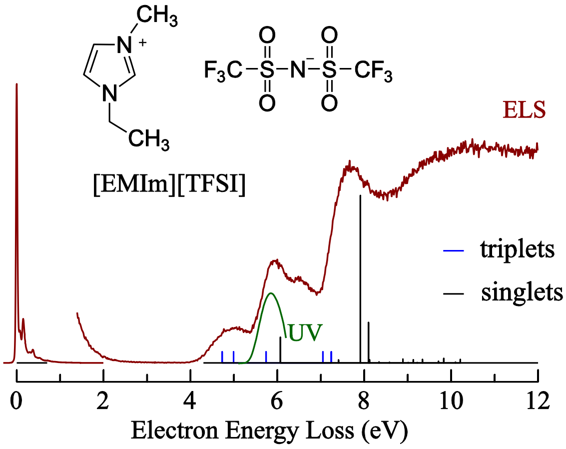

Figure 2. Sample EEL, UV and DFT/MRCI spectra.

Excited states of four representative ionic liquids were characterized by electron energy-loss spectra (EELS) and DFT/MRCI calculations, with good agreement. The capacity of EELS to induce spin-forbidden transitions revealed triplet states. Bands in the 3-8 eV range were assigned to (π,π^*) transitions of the cations; anion states are at energies above 7 eV. The spectrum of the piperidinium cation is ‘empty’ in the energy-loss range 2-8 eV, reflecting the absence of a (π,π^*) system.

Energy-loss spectrum of saturated solution of methylene green in [EMIm][BF_4] showed a methylene green band at ΔE = 2 eV, demonstrating that ionic liquids may serve as hosts for nonvolatile compounds. Surprisingly, the methylene green band was missing in the energy-loss spectrum when it was dissolved in a different IL, [BMPipe][TFSI] – this may indicate that it is displaced from the surface and cannot be reached by electrons as they have a limited penetration depth. This demonstrates the power of EELS to study surface structure.

Interface wettability properties of 11-mercaptoundecanoic acid SAMs

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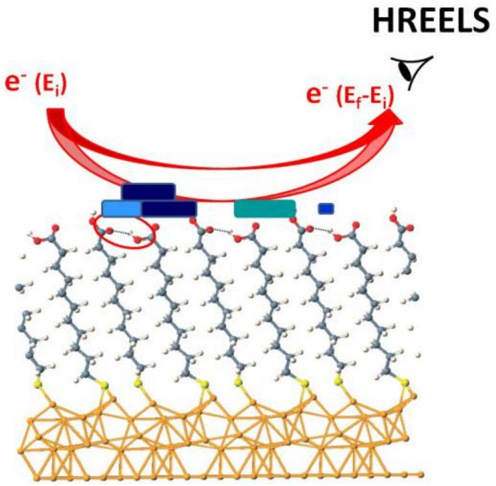
Self-assembled monolayers (SAMs) have been proposed as molecular platforms for the development of chemical devices, such as chemical or biological sensors [1]. In this context, it is of primary importance to control hydrophilic/hydrophobic character of the prepared interfaces [2], and to characterize their interaction with water.

We present a study on the wetting of a model acid terminated alkanethiolate system: in 11-mercaptoundecanoic acid (MUA, HS-$(CH_2)_{10}$-COOH) SAMs deposited on gold, the terminal functions are hydrogen bonded [3,4]. These SAMs were exposed to water H_2O at cryogenic temperature (~28 K) and eventually further annealed below water desorption temperature (see scheme). The wettability properties at the water/SAM interface were studied by means of High Resolution Electron Energy Loss Spectroscopy (HREELS). This vibrational analysis technique is particularly well-adapted for characterizing species present in very low amounts because of its intrinsic surface sensitivity. The formation of the wetting film and its completion were investigated, in particular by following the evolution of the ν(OH) stretching band when exposing the SAMs to increasing low (< 5 L) doses of water H_2O [5].



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A side-by-side comparison of comprehensive gas phase, surface, and *in-situ* studies of two FEBID precursors: $MeCpPtMe_3$ and π-$C_3H_5Ru(CO)_3Br$

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Focused electron beam induced deposition (FEBID) is a direct-write nanofabrication technique currently limited in resolution due to deposition outside the area of the primary electron beam and in metal purity due to incomplete precursor decomposition. Both limitations are partly caused by interactions of precursor molecules with low-energy secondary electrons, which are abundant both inside and outside the area of the primary electron beam and are associated with reactions causing incomplete ligand dissociation from FEBID precursors. As it is impossible to directly study the effects of secondary electrons *in situ*, we must use other means to elucidate their role. Gas phase studies examine low-energy electron-induced reactions with FEBID precursors by studying isolated molecules interacting with single electrons of well-defined energy. UHV surface studies on adsorbed precursor molecules probe surface speciation and species desorption from the substrate during electron irradiation under conditions more representative of FEBID. Comparing these two types of studies with *in situ* FEBID experiments, allows insight into the primary deposition mechanisms for individual precursors; ideally, this information can be used to design future FEBID precursors and optimize deposition conditions.

This pair of posters compares gas phase, surface, and *in situ* FEBID experiments performed on the recently-examined organometallic candidate precursor π-$C_3H_5Ru(CO)_3Br$ with similar experiments performed previously on MeCpPtMe3, a FEBID precursor known to produce deposits from 20 atomic % purity up to 92 atomic % purity with post-deposition processing. This experimental methodology is used to suggest potential low-energy electron-induced process leading to deposition for each of these precursors, including dissociative electron attachment (DEA) and dissociative ionization (DI).

Acknowledgements: This work is supported by the Icelandic Research Fund (RANNÍS) and the University of Iceland Research Fund. This work was conducted within the framework of the COST Action CM1301 (CELINA) and RT acknowledges a STSM support from CELINA.

Amplification of electron attachment induced fragmentation through new bond formation as a possible rout in precursor design.
Part I; CO and F_2CO formation from tetrafluoro-para-benzoquinone.

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This contribution is the first of two demonstrating extensive fragmentation in DEA that is enabled through rearrangement and new bond formation. Such extensive fragmentation, fueled by new bond formation, is not uncommon in DEA and may offer a route for ligand design that enables precursor molecules to undergo a more complete fragmentation in lieu of the single ligand loss commonly observed in DEA to current FEBID precursors. The motivation behind these poster presentations is to open up the discussion on the feasibility of this approach to favorably direct low energy electron induced fragmentation in FEBID precursors.

In this “first part”, we summarize results from electron attachment to tetrafluoro-*para*-benzoquinone (TFQ), which we have discussed in detail elsewhere [1]. While the metastable molecular anion is observed at incident electron energies well above 0 eV, dissociative electron attachment (DEA) leads to a distinct fragmentation pattern which we discuss here in relation to our calculations of the respective thermochemical thresholds. The observed fragmentation reactions can largely be described through two dissociation series: the formation of $[TFQ - CO - nF]^-$ (n = 0-3) and the formation of $[TFQ - 2\,CO - nF]^-$ (n = 0-4). While the channels where n = 1 or 3 are fairly inefficient in the first series, the loss of CO and two fluorines is an efficient channel. This effect can be attributed to the formation of the stable difluoro formaldehyde, F_2CO molecule. Though less pronounced, this is also true for the loss of two CO and two fluorines in the second series, which is attributed to the formation of CO and F_2CO. The most striking DEA channel from TFQ, observed at incident electron energies as low as ~2.7 eV, is thet leading to the formation of C_4^-. This may be attributed to the formation of two neutral F_2CO molecules and recombination of the remaining moiety to form an anionic 4-carbon chain.

Acknowledgement: The authors acknowledge support from the Icelandic Centre for Research and the University of Iceland Research Fund.

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Amplification of electron attachment induced fragmentation through new bond formation as a possible rout in precursor design.
Part II; HF and CO formation from ortho- and para-tetrafluorohydroquinone.

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This contribution is the second of two demonstrating extensive fragmentation in DEA that is enabled through rearrangement and new bond formation. Such extensive fragmentation, fueled by new bond formation, is not uncommon in DEA and may offer a route for ligand design that enables precursor molecules to undergo a more complete fragmentation in lieu of the single ligand loss commonly observed in DEA to current FEBID precursors. The motivation behind these poster presentations is to open up the discussion on the feasibility of this approach to favorably direct low energy electron induced fragmentation in FEBID precursors.

In this "second part", we discuss dissociative electron attachment to *ortho*-tetrafluorohydroquinone (*o*-TFHQ) and *para*-tetrafluorohydroquinone (*p*-TFHQ) in conjunction with quantum chemical calculations on the reaction paths and activation barriers involved. Both *o*-TFHQ and *p*-TFHQ capture electrons through two distinct low-energy resonances, which result in maxima in the dissociative electron attachment (DEA) ion yield close to 0 and 1.5 eV. In both cases complex rearrangement reactions involving multiple bond ruptures and new bond formations are observed, i.e., reactions that are energetically enabled by the formation of highly stable neutrals such as HF and CO.

The dominating DEA channels are the spontaneous loss of one or two HF molecules, leading to $[M - HF]^-$ and $[M - 2\,HF]^-$, respectively. The former channel is observed for both molecules at close to 0 and at 1.5 eV, although with distinctly different branching ratios. The formation of $[M - 2HF]^-$ is also observed through both resonances from *p*-TFHQ; however for *o*-TFHQ this channel only proceeds through the higher lying resonance. In addition, a considerable contribution to the ion yield from *o*-TFHQ is observed through the loss of both HF and CO (formation of $[M - HF - CO]^-$) close to 1.5 eV. This channel barely exists for *p*-TFHQ. This is readily explained by our calculations showing that the respective activation barriers govern the HF loss, while the loss of CO and HF from *o*-TFHQ is enabled by a proton-shuttling mechanism that is not possible for *p*-TFHQ.

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Electron Induced Reactions in Fluorinated Acetamide and its Methyl Ester

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The investigation of the interaction between electrons and neutral molecules is of high importance in both fundamental sciences and application such as radiation chemistry, chemistry of the upper atmosphere, plasma physics and material science [1]. In many industrial applications dissociative processes generating reactive radicals are of great importance. Among them dissociative electron attachment (DEA) plays a particular role as this process can be dissociative at electron energies considerably below the dissociation energy of the corresponding chemical bond. DEA has been studied so far in many compounds especially in halogenated molecules due to their pronounced electron scavenging properties. Prototype electron scavengers are the chlorofluorocarbons (CFCs) with their pronounced electron scavenging properties. While they are photochemically very stable they are very sensitive towards electrons with almost no excess energy. The extra electron can enter the lowest unoccupied orbital of the σ*(C-X) character (where X is a halogen atom) hence the transient negative ion (TNI) directly decomposes along a repulsive potential energy surface.

Here we present results on dissociative electron attachment to halo-substituted acetamide (CF_3CONH_2) and its methyl ester ($CF_3CONHCH_3$). We have found that these molecules are very sensitive towards low energy electrons, *i.e.*, they possess low energy resonances leading to an effective decomposition of the molecule. The involved MOs have $\pi^*(CONH_2/CONHCH_3)$ character and the subsequent decomposition reactions are very complex involving substantial rearrangement in the TNI resulting in multiple bond cleavages and the formation of new molecules. We compare direct DEA reactions with the presently observed indirect reactions in terms of their selectivity to cleave specific bonds in order to form particular products.

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Gas phase dissociative electron attachment and dissociative ionization of 1,1-dichloro-1-silacyclohexane, silacyclohexane and 1,3,5-trisilacyclohexane; comparison of the performance of these molecules in FEBID

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In the current contribution we present previously published dissociative electron attachment and dissociative Ionization data on 1,1-dichloro-1-silacyclohexane (DCSCH), silacyclohexane (SCH) and current data on 1,3,5-trisilacyclohexane (TSCH). These compounds show very different behavior with regards to the relative efficiency for DEA vs. DI. In an attempt to shed some light on the relative effect of these dissociation channels on the lateral resolution in Focused Electron Beam Induced Deposition (FEBID) we have also studied deposit broadening and the proximity effect when these molecules are used as precursors for the fabrication of nano-pillars in FEBID.

In gas phase studies [1] we have shown that DCSCH has fair cross section for DEA as well as DI, while SCH is apparently 'inert' towards DEA. For TSCH we expect similar behavior as has been observed for SCH. These compounds are thus good candidate to study the relative effect of DEA vs. DI in FEBID. For this purpose we grew series of nano-pillars using DCSCH and TSCH with increasing electron beam exposure time. The base diameter of the nano-pillars grown with TSCH is saturating much sooner (at ~97nm) than the base diameter of nano-pillars grown with DCSCH (at 160nm). Similarly the diameter of neighboring pillars, in close proximity to growing pillars, is found to be stronger influenced (broadened) in DCSCH compared to SCH.

In the current contribution we discuss these FEBID results in context to the efficiency of DI and DEA to these compounds in the gas phase.

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Electron Induced Reactions of Iron Carbonyl Complexes

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Using the crossed electron/molecular beams technique [1] equipped with a trochoidal electron monochromator and quadrupole mass spectrometer we have investigated the low energy electron collisions with iron carbonyl complexes. First the electron induced ionization of iron pentacarbonyl molecule was done [2], the present research is focused on electron induced ionization of diiron nonacarbonyl molecule and its comparison with the results of iron pentacarbonyl. Both complexes are typical with the sequential loss of CO ligands, as for the $Fe(CO)_5$ the strongest feature in the mass spectrum are the $Fe(CO)_n^+$ fragments with n=4…0, in the mass spectrum of $Fe_2(CO)_9$ the $Fe_2(CO)_m^+$ ions can be identified with m=8…4. Below the mass of $Fe(CO)_5^+$ at m/z 196 no new ionic fragments were identified in the spectrum of $Fe_2(CO)_9$ different from those detected in the spectrum of $Fe(CO)_5$ [2]. The production of the same $Fe(CO)_n^+$ fragments results in higher ion yields than in the spectrum of $Fe(CO)_5$ [2], without contribution from other possible products with two iron atoms included, like $Fe_2(CO)_3^+$ at m/z 196 with $Fe(CO)_5^+$ or $Fe_2(CO)_2^+$ at m/z 168 together with $Fe(CO)_4^+$. Moreover no doubly charged products of $Fe_2(CO)_9^+$ and its fragments with two iron atoms were detected, as well as no CO bond breaks for $Fe_2(CO)_m^+$ fragments occurred contrary to those known from the spectrum of $Fe(CO)_5$ [2], like $FeC(CO)^+$, FeC^+, $FeC(CO)^{2+}$ and FeO^+.

This work was supported by the Slovak Re-search and Development Agency under Contract No. APVV-0733-11 and the VEGA V/0514/12 project. This work was conducted within the framework of the COST Action CM1301 (CELINA).

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Electron Impact Excitation of the Bismuth Resonance Line

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Electron scattering by bismuth atom has been of recent interest regarding the excitation of autoionising states [1] and the presence of Bi lines in so called CP (chemically peculiar) stars [2].

We have performed the measurements of differential cross sections (DCS) for the excitation of the $6p^2 7s$ $^4P_{1/2}$ state of bismuth using the electron spectrometer ESMA [1]. Effusive beam of bismuth atom was perpendicularly crossed by monochromatic electron beam and the yield of scattered electrons was determined. Before each measurement the energy loss spectrum was obtained in order to check for the presence of dimmers (Bi_2). After applying the effective length correction factor, relative DCS were put on the absolute scale by normalization to the optical oscillator strength of 0.146 of the resonance bismuth transition. By extrapolating DCS in the angular range toward zero and 180° angles, the integral, momentum transfer and viscosity cross sections have been determined.

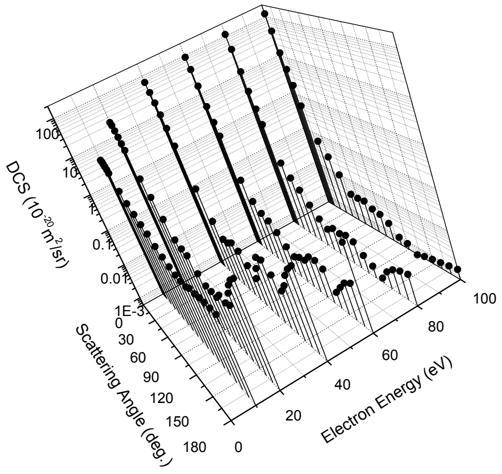

Figure 1. *Differential cross sections of electron impact excitation of the* $6p^2 7s$ $^4P_{1/2}$ *state of bismuth in units of* 10^{-20} m^2/sr *at incident electron energies of 10, 20, 40, 60, 80 and 100 eV and scattering angles from* 2° *to* 150°. *Data points out of this range are extrapolated values.*

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Low-energy electron interactions with tungsten hexachloride

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Tungsten hexachloride (WCl_6) was often used as a precursor in electron beam induced dissociation (EBID) to obtain structurally well-defined metal containing nanostructures [1]. However, the purity of the produced layers is still far of what it is desirable, which influences some of the properties (e.g. resistivity) and function of the created surface. The origin of the impurities can be assigned to many factors, i) the presence of precursor fragments, ii) incomplete precursor dissociation, etc. [2].

One of the reaction products in the interaction of the primary energetic electron beam with the surface are secondary electrons with low energy (LEE). These secondary LEEs have a kinetic energy distribution typically up to 15 eV and can have a considerable role in the deterioration of the spatial resolution of the technique referred above [3]. Thus, studies of the interaction of LEEs with such compounds are important to have a full understanding on the processes that are occurring during beam deposition.

In this contribution a double focusing mass spectrometer was used to perform electron ionisation and dissociative electron attachment to WCl_6 in the gas phase. The molecule shows strong fragmentation in terms of the loss of Cl ligands. It is possible to observe the presence of the WCl_n^+ (n=0 – 4) series as well as the WCl_nO^+ (n=0 – 5) series. The latter ions were observed due to oxidation of the sample. No parent or oxidized parent were observed. When performing dissociative electron attachment to WCl_6, the following fragments were observed: Cl^- (35 u), WCl_2O^- (270 u), WCl_3^- (291 u), WCl_3O^- (307 u), WCl_4^- (326 u).

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Electron Induced Fluorescence as a Tool for Studying Precursor Dissociation

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During the deposition process induced by electron beam relatively large amount of secondary and backscattered electrons with low energies is generated [1]. These are mainly responsible for unwanted radial growth and partially for the contamination of the deposited structure. Their energies are well above the thresholds for different dissociation processes causing depositing of incompletely dissociated fragments of the precursor molecule. The electron induced dissociation processes are usually studied in the cross beam experiments in the gas phase where the produced ions are detected by means of mass spectrometry [2]. This approach provides information on charged fragments but not neutral products. The electron induced fluorescence, on the other hand, using optical spectrometry detects excited species which can be both neutral or charged and apart from determining excited fragments the dissociative excitation cross sections can be measured as well. The example of the dissociative excitation efficiency curve is shown in the figure. It corresponds to the deexcitation of the iron atom produced in the electron collision with iron pentacarbonyl [3].

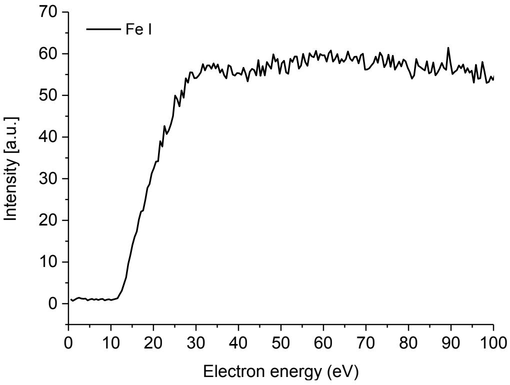

Fig. 1. Dissociative excitation efficiency curve for Fe I transition at 372 nm produced by electron impact on $Fe(CO)_5$.

This study was partially supported by the Slovak Research Agency, project No. APVV-0733-11, DO7RP-0025-1. This work was conducted within the framework of the COST Action CM1301 (CELINA).

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Absolute cross sections for electronic excitation of pyrimidine

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Electronic excitation is an important process for FEBIP as it is the first step of neutral dissociation, which is much less studied in contrast to DEA. Pyrimidine was chosen because it is an important molecule since DNA and RNA bases are pyrimidine derivatives. Electron scattering from pyrimidine has been studied in the past both experimentally [1-3] and theoretically [4-6], however there are still open questions.

We measured absolute differential cross sections (DCS) for elastic scattering and for electronic excitation of five electronically excited states of pyrimidine (shown on Figure 1) at 0°, 45°, 90°, 135° and 180°, then integrated them over angle and received integral cross sections. One example of energy dependence spectrum – excitation of the state at $\Delta E = 4.26$ eV (see Figure 2) shows three clear bands which must be due to $^{2}(\pi, \pi^{*2})$ core-excited shape resonances.

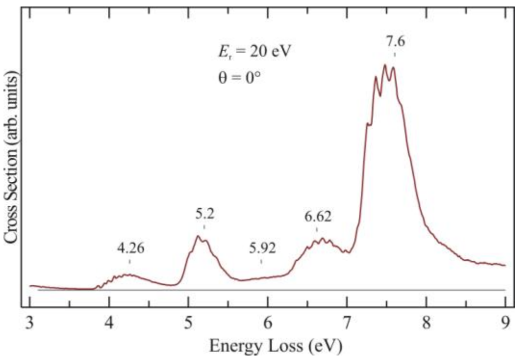

Figure 1. EEL spectrum of pyrimidine.

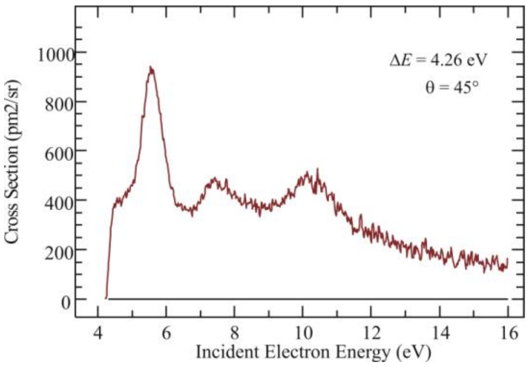

Figure 2. DCS for exciting the state at ΔE=4.26 eV.

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Two-dimensional spectra of electron collisions with acrylonitrile and methacrylonitrile reveal nuclear dynamics

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We have measured the elastic and vibrationally inelastic differential cross sections of acrylonitrile (in absolute units) and methacrylonitrile (relative units) at a scattering angle of 135°. In the energy dependence spectra of vibrational excitation of acrylonitrile the bands at 2.9 and 4.4 eV were observed which must be due to shape resonances, at low energy sharp structures were found, they are due to either boomerang structure of a shape resonance or vibrational Feshbach resonances.

Acrylonitrile is a suitable target to study the coexistence of the dipole-bound and the valence states of the anion because electron transmission spectroscopy revealed sharp structures – narrow resonances – in electron scattering at low energy [1] and it was shown that acrylonitrile due to its large dipole moment (3.86 D) supports dipole-bound states [2].

We measured methacrylonitrile hoping that it can help us to define the nature of the first resonance in acrylonitrile and assign it to either a shape resonance or vibrational Feshbach resonance because it is known that a methyl substituent destabilizes the π^* orbitals by hyperconjugation, shifting the shape resonance up by 0.1–0.2 eV. The first resonance in methacrylonitrile appeared shifted up by about 0.1 eV compared to acrylonitrile, proving that it has to be a simple shape resonance.

The detailed view of the autodetachment dynamics is gained from a two-dimensional electron impact spectrum, in which cross section is plotted as a function of the incident electron energy, which determines the initial state of the negative ion, and of the energy loss, which carries information about the final state of the neutral molecule. The 2D spectrum of acrylonitrile reveals diagonal patterns [3], which are also observed in methacrylonitrile, although they become much broader, indicating that the methyl group substantially shortened the resonance lifetime.

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Electron Induced Fluorescence Study of Iron Pentacarbonyl: Iron Atom Lines

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The investigation of the excitation reactions of Fe(CO)$_5$ induced by electron impact was performed using Electron Induced Fluorescence Apparatus in two modes: UV/VIS emission spectrum measurement, and photon efficiency curves recording for particular spectral lines (Figure 1). The emission spectrum at 50 eV electron impact energy was dominated by Fe I emission lines. The Fe I emissions relate to dissociative excitation of Fe(CO)$_5$, leading to removal of all CO ligands from the molecule and subsequent Fe excitation to different excited states.

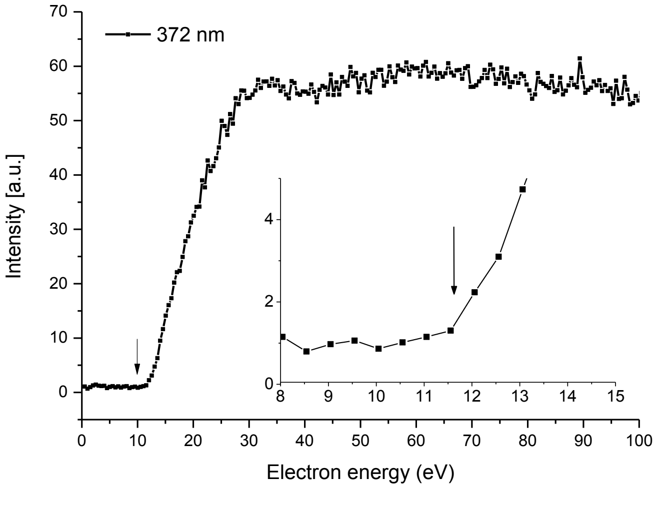

Figure 1. Photon efficiency curve recorded at 372 nm and ascribed to the Fe I transition w^{5}F° (4) → a^{5}P (3) originating from Fe(CO)5.

Acknowledgement

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Electron Induced Fluorescence Study of Iron Pentacarbonyl: Carbonyl Bands

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Dissociative excitation processes and dissociative ionization with excited products of iron pentacarbonyl $Fe(CO)_5$ were studied equipping electron induced fluorescence method. Fluorescence spectrum was recorded at the electron energy of 50 eV in the range of 200-470 nm. It was dominated with Fe I and Fe II lines with the presence of CO I and CO II band lines. The spectral lines were spaced closely and often mixed. The focus was laid on the carbonyl CO emission and photon efficiency curves we measured. More than one threshold was usually detected, resulting from the line mixing. Mechanisms and energetics of the dissociative processes leading to the emission of CO bands were discussed.

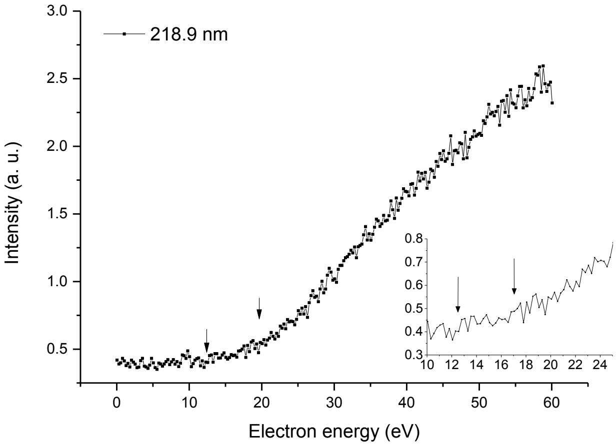

Figure 1. Photon efficiency curve obtained at 218.9 nm with two thresholds corresponding to Fe I (~12.5 eV) and (0,0) band of the first negative system of CO (CO II $B^2\Sigma^+ \rightarrow X^2\Sigma^+$) (~20 eV) transitions originating from $Fe(CO)_5$.

Acknowledgement

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Electron Beam Induced Surface Activation as a Means to Study Fundamental Aspects of Electron Scattering Processes

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Electron scattering in matter is a fundamental process observed in practically all applications involving energetic electron beams. Backscattered (BSE) and forward scattered (FSE) electrons (and the thereby induced secondary electron emission) can cause unintended electron induced reactions, like deposition or etching. These so-called proximity effects usually lead to enlarged deposits and thus hamper the fabrication of well-defined nanostructures. In conventional electron beam induced deposition (EBID) it is impossible to study the FSE and BSE proximity effects independently, as deposited material creates forward scattering centers.

In order to address this issue, Electron Beam Induced Surface Activation (EBISA) [1, 2] was used to gain insights exclusively into the BSE effects. In EBISA, a surface is irradiated with the focused, high energy electron beam under vacuum conditions (HV or UHV), resulting in surface activation. In a second step, a suitable precursor, e.g. iron pentacarbonyl $Fe(CO)_5$ [1], is dosed onto the surface and selectively dissociates at the pre-irradiated, activated surface areas. In a third step, the initial deposit may continue to grow due to autocatalytic decomposition upon prolonged precursor dosage and form clean Fe nanostructures. As no deposit is formed during the irradiation, only BSEs have to be considered.

We studied the EBISA on different substrates, e.g., SiO_2 and TiO_2, using $Fe(CO)_5$ as a standard precursor and also found that also thin organic films (few molecular layers) can be activated by electrons [2]. A single closed layer of molecules is sufficient to suppress the reactivity of intrinsically active substrates like Ag(111), while molecules in the second and higher layers are effectively decoupled from the substrate surface and can be successfully activated by the electron beam [2].

Using ultrathin films of 2H-tetraphenylporphyrin (2HTPP) on different substrates as layers to be activated [2], we are able to effectively separate the electron scattering properties of the substrate from the chemical processes that are responsible for the activation. This allows us to study the support material dependent proximity effects as well as the activation mechanism in detail for the 2HTPP/$Fe(CO)_5$ system. The experimental results are complemented by electron scattering simulations to elucidate the role of the BSE dose, current density and energy.

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Fabrication of carbon-free cobalt nanostructures on porphyrin-covered $TiO_2(110)$ using the precursor $Co(CO)_3NO$

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The fabrication of nanostructures with a defined elemental composition is a major challenge in Focused Electron Beam Induced Processing (FEBIP). We demonstrate in analogy to recent FEBIP experiments with $Fe(CO)_5$ on Ag(111), pre-covered with thin layers of 2H-Tetraphenylporphyrin (2HTPP), in UHV [1], that it is possible to fabricate carbon-free Co deposits on rutile $TiO_2(110)$ also pre-covered 2HTPP. One 2HTPP layer effectively hinders $Co(CO)_3NO$ from decomposing unselectively on the pristine $TiO_2(110)$ surface. In a first step, Scanning Tunneling Microscopy was employed to ensure 2HTPP forms a closed layer. The Co deposition process is then realized either via Electron Beam Induced Deposition (EBID), or Electron Beam Induced Surface Activation (EBISA) [2]. In EBISA, the 2HTPP layer is irradiated in the absence of the precursor, leading to active sites where catalytic deposition occurs once the precursor is dosed onto the surface. We thus demonstrate for the first time that EBISA is a viable method to fabricate Co deposits from $Co(CO)_3NO$. All deposits show a distinct contrast in Scanning Electron Microscopy between the central part and the periphery of the corresponding structures. Local Auger Electron Spectroscopy reveals that the central part consist only of cobalt, nitrogen and oxygen, whereas the periphery exhibits a significant carbon content. Furthermore, we demonstrate that additional dosage of $Fe(CO)_5$ on these structures leads to its decomposition and subsequent autocatalytic growth of pure bcc Fe only in the central part, whereas the periphery is unaffected. This selectivity is attributed to the higher Co purity of the central part.

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Novel insights into the water-assisted purification of FEBID deposits produced from $MeCpPtMe_3$

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The widely applied FEBID precursor trimethyl(methylcyclopentadienyl)-platinum(IV) ($MeCpPtMe_3$) is renowned as a notoriously bad precursor because it typically yields deposits with Pt content of only about 20% [1,2]. Fundamental studies have identified the reason for the low Pt content of FEBID deposits produced from $MeCpPtMe_3$. It was found that DEA predominantly leads to loss of only one CH_3 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_3 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 the 'notoriously bad' precursor $MeCpPtMe_3$ can be efficiently purified by a post-deposition electron-beam treatment in the presence of water vapour thus yielding a 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_2, CH_x). This contribution presents 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 $MeCpPtMe_3$. The results give insight into the chemistry underlying the previously reported deposit purification process [5].

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Synthesis and characterization of heterometallic carbonyls for focused electron beam induced deposition

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Homometallic carbonyls are widely used precursors for nanomaterial synthesis in gas phase processes and in liquids to form metallic coatings or nanostructures. Many of these carbonyls are commercially available and therefore they have been extensively studied. In particular, the deposition of metallic nanostructures by focused ion beam deposition (FEBID) using these homometallic carbonyls has been investigated and optimized in the recent past.[1-3] To date, deposition of more than one metal is limited to the co-feeding of multiple gaseous sources despite synthetic methods to prepare heterometallic carbonyls.

As a proof of concept, $HFeCo_3(CO)_{12}$ was prepared from the homometallic $Fe(CO)_5$ and $Co_2(CO)_8$ in a slightly modified procedure described by Chini *et al.*.[4] The heterometallic carbonyl was recrystallized to obtain suitable single crystals, which were used to solve the crystal structure for a simulation of the powder XRD pattern to yield information about a larger sample size. $HFeCo_3(CO)_{12}$ can be sublimed at temperatures below 60 °C (10^{-2} mbar) and decomposes to a smooth metallic film in a low pressure chemical vapour deposition with an expected metal ratio of 1:3.02 (Fe:Co) according to EDX analysis. This heterometallic carbonyl precursor was used in a FEBID process yielding deposits with high metal contents after optimisation of the process parameters.[5] The FEBID investigations will be highlighted in another contribution by Michael Huth *et al.*.

This work was conducted within the framework of the COST Action CM1301 (CELINA).

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Synthesis and thermal behavior analysis of new yttrium beta-diketonate precursors for investigation as a chemical vapor deposition

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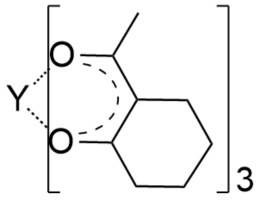
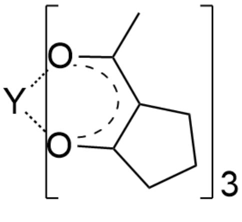
Yttrium MOCVD precursors of type Y[ach]$_3$ (Hach= 2-acetylcyclohexanone), Y[acp]$_3$ (Hacp= 2-acetylcyclopentanone) and Y[dp]$_3$ (Hdp= 1,3-diphenyl-1,3-propandione) have been prepared by the reaction of yttrium nitrate with the respective β-diketonates at ambient temperature.

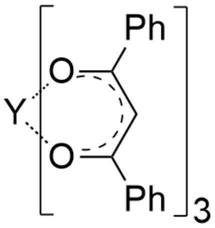
The thermal decomposition of the complexes was studied by TG, DSC and TGMS experiments. Vapor pressure measurements were carried out over a temperature range of 333–700 K. The phase purity of the obtain materials was analyzed by powder X-ray diffraction, showing the formation of pure Y_2O_3. The obtained data are compared with literature known β-diketonate yttrium precursors, such as Y(thd)$_3$ (thdH = 2,2,6,6 tetramethyl-3,5-heptandione)[1]



Y(ach)$_3$



Y(acp)$_3$



Y(dp)$_3$

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Chemical Vapor Deposition of Conformal Phosphorus-doped Ruthenium Layers

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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 of ruthenium precursors of general type $Ru(CO)_2(P^nBu_3)_2(O_2CR)_2$ (R = Me, Et, ^{i}Pr, ^{t}Bu, CH_2OCH_3, CF_3) and their use as single-source CVD precursors for the preparation of thin and conformal phosphorus-doped ruthenium layers. Variation of the carboxylate ligands allowed influencing the thermal behavior and vapor pressure of the respective precursor. All ruthenium precursors are well suited for the deposition of conformal and dense phosphorus-doped ruthenium layers without addition of any reactive gas by applying the MOCVD process. The obtained layers were characterized by SEM, EDX, AFM and XPS measurements.

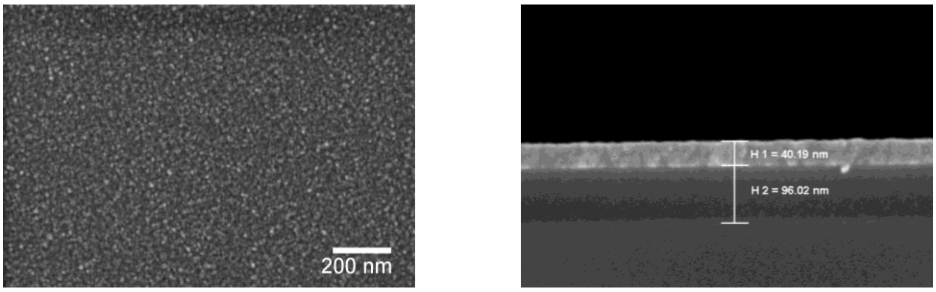

Fig. 1: SEM images of a phosphorus-doped ruthenium layer generated from $Ru(CO)_2(P^nBu_3)_2(O_2CCH_2OCH_3)_2$.

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Platinum purification for higher conductive contacts for individual SnO2 NWs gas sensor

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Electron-beam induced Platinum deposition from $C_5H_4CH_3Pt(CH_3)_3$ precursor, usually employed in dual-beam FIB machines, has the main disadvantage of high carbon content, which gives rise to a low conductivity of the fabricated Pt nanostructures. A postprocessing of this nanostructure for diminishing its resistivity by about 5 orders of magnitude, as proposed by Mehendale et al. [1] and Villamor et al. [2], consists in applying high local oxygen flow close to the deposit while the electron beam is irradiating it, either heating the structure at 120ºC or keeping it at room temperature, respectively.

On the other hand, individual SnO_2 nanowires have been implemented as a gas nanosensor for detecting the presence of toxic gases [3], contacting them by electron and ion beam induced Pt deposition. Due to the high resistance of Pt, part of the power supplied to the nanodevice for its operation is lost in the Pt accessing contacts.

In this work, a combination of both methodologies has been attempted, consisting in SnO_2 NWs that have been contacted by purified electron beam induced Pt structures with the above mentioned approach. 4 probes electrical measurements show very low resistivity in the range of $10^2 \mu\Omega\cdot$cm, which is 2 orders of magnitude lower than other SnO_2 structures reported [4]. Ohmic behavior is obtained in 2-contacts I-V curves for all contacted NWs, which is related to the high conductivity of the NWs.

The devices have been tested towards UV light exposure, showing response and decay times in agreement with other experimental values for metal oxide nanowires. The gas sensing has been monitored towards the presence of NO_2, CO and NH_3 in synthetic air, and no gas response has been observed. Possible explanation is that the surface of the metal oxide NWs might be affected by the purification process, causing the adsorption of oxygen molecules by chemisorption with high activation energy that were not desorbed with UV light.

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Spatial resolution of EDX for the detection of nanostructures

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Electron Beam Induced Deposition (EBID) is a direct-write lithography technique that provides sub-10 nm resolution. The dissociation of the precursor gas by the electron beam leads to deposition of structures of sizes in the sub-10nm range. Energy Dispersive X-ray Analysis (EDX) can play a crucial role in analyzing the composition of structures when developing novel gas precursor, but also when using EBID, to pattern devices with sizes in the sub-10 nm range. The spatial resolution of EDX can be determined from a line-scan over a sharp interface and has been reported in [1] to be as low as 40±10 nm. This study aims at the determination of the smallest detectable structure by EDX. When using bulk samples, the spatial resolution of EDX is strongly influenced by the electron-sample interaction volume. It is known that lowering the acceleration voltage decreases the interaction volume, but also the spatial resolution. Our setup consists of a FEI Nova Nano Scanning Electron Microscope (SEM), equipped with a silicon drift EDX detector (SDD). We demonstrate that 15 nm Gold NanoParticles (AuNP) can be detected on a Silicon bulk substrate, at 7.5 kV and 0.47 nA, as shown in Fig.1. When using thin film grids, however, the interaction volume is limited by the thickness of the film, hence a higher acceleration voltage can be used. We succeeded in detecting AuNP's with sizes down to 3 nm on top of a Carbon film, at 17.5 kV and 2.3 pA, as shown in Fig.1. In Fig. 2 an EDX map is shown of these particles, at 20 kV and 0.6 nA beam. Note that the EDX map also reveals AuNP's on the backside of the film, invisible in the SE image.

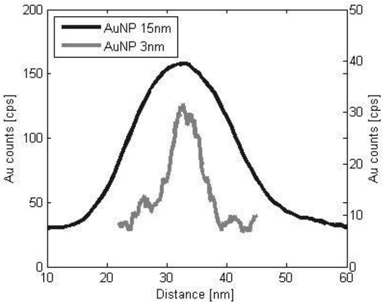

Fig.1 15nm and 3nm AuNP linescan

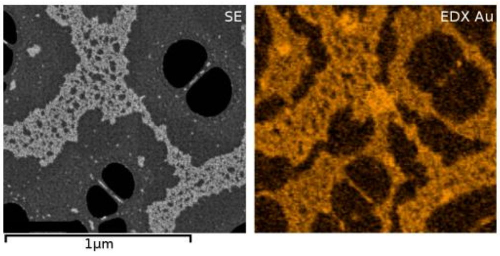

Fig. 2 3nm SEM image (left) and EDX map (right)

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Gas Assisted Etching of High Density Polyethylene (HDPE) for the Development of Functional Surfaces

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Polymers are highly susceptible and very much prone to react on electron and ion beam irradiation where the effect is even higher when the ions are used as incident particles and the end-effect might even be the total loss of the material properties. Especially, controllable surface modification allows tuning of surface properties in intended directions and thus provides the use of the ultimate materials and their systems towards desired and pre-defined targets out at the micro/nano-scale for creating functional surfaces. The current work mainly focuses on using gas injections systems (GIS) in the FIB-SEM instrument to combine gallium beam irradiation effects with gas assisted etching (GAE) to optimize, design and develop new polymer surface properties and create functional polymer surfaces that can be utilized for different fields of science and technology. For GAE experiments in this work, XeF_2 and I_2 gases were used in addition to gallium ion etching of High Density Polyethylene (HDPE) surfaces with different beam currents and accordingly different gas exposure times resulting at the same ion fluences. The alterations in the surface morphologies due to gas assisted etching based nano-structuring with various processing parameters were tracked using HR-SEM imaging and Atomic Force Microscopy (AFM) investigations.

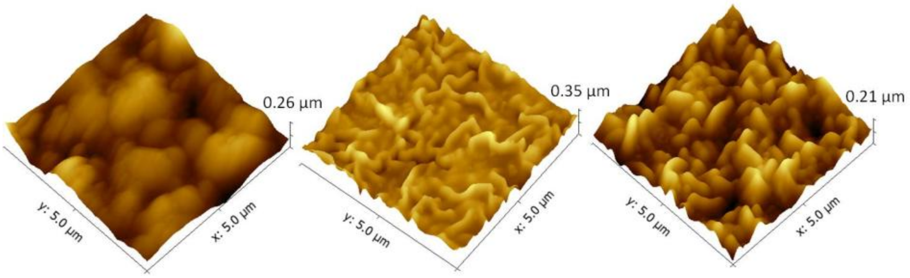

Figure 1. 3D AFM images of the I_2 assisted ion beam etched surfaces with 3 nA, 5 nA and 7 nA, from left to right, respectively

*The authors gratefully acknowledge the support by TUBITAK 114M040 project and CM 1301 (CELINA) COST Action

In-situ controlled Focused Electron Beam Induced Etching of semiconductor nanowires

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Silicon and germanium nanowires have received increasing attention due to their applications in advanced field effect nanodevices [1], thermoelectric devices [2], and sensors. A controlled tuning of the diameter and of the roughness is essential for these applications. Here we address the challenge of modifying the nanowire to investigate changes of its electrical characteristics.

Focused electron beam induced etching is a direct write novel nanofabrication approach which can be used to tune the nanowire properties. In this technique, an electron beam with a beam current above 1nA was used to modify the silicon or germanium surface in the presence of an etch gas. In this work, chlorine will be used as etch gas to etch silicon or germanium nanowires (Fig. 1). Various beam, scanning and etching parameter are involved in the FEBIE process. In this work, acceleration voltage, electron dose, exposure time will be varied to study the effect of these parameter on the etching process. The impact on the etch rate and the surface roughness of nanowires will be discussed. Morphological and structural analysis of the nanowires performed with the transmission electron microscope show that the crystallinity has been retained.

To conclude, focused electron beam induce etching is a versatile approach to thin semiconductor nanowire properties. Potential applications of FEBIE based nanodevices for sensor applications will be discussed.

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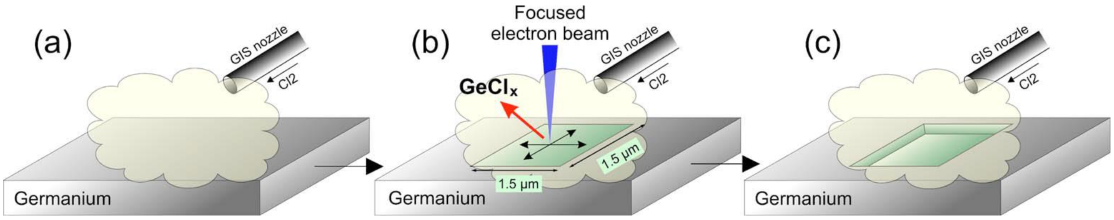

Figure 1: Schematic diagram of etching process on germanium

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Purification of Electron Beam Induced Deposited Gold Nanostructures

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Focused electron beam induced deposition (FEBID) from volatile organometallic precursors is a mask- and resist-free direct write technology also suitable for the deposition of noble metal structures. Especially gold nanostructures have been of recent interest due to the vast range of potential applications comprising nanoplasmonics, biomolecule devices and nanowire transistors. All these applications are hindered by the low metal content currently achieved in deposits [1]. Our investigation of selected experimental FEBID parameters yields insight to the achieved structure and composition of the deposits. Furthermore an oxygen plasma purification technique to improve metal content which also conserves the shape of the deposited structures is investigated.

In summary this work will discuss approaches to improve the gold content of FEBID structures by a combination of optimized deposition parameters as well as the use of an ex-situ plasma purification step.

The research leading to these results has received funding from the European Community´s Seventh Framework Programm (FP7/2007-2013) under Grant number ENHANCE-238409. We would also like to thank the Cost Action CM1301 on Chemistry for Electron-Induced Nanofabrication for the support.

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MFM and TEM analysis of Co square magnetic rings

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Square rings made up of 1 μm long, 80 nm wide and 45 nm thick nanowires have been fabricated by focused electron beam induced deposition (FEBID) of Co-carbonyl ($Co_2(CO)_8$) precursor. The structures were deposited on Si and C-grid substrates for magnetic force microscopy (MFM) and transmission electron microscopy (TEM) analysis, respectively. MFM measurements, performed after applying a 0.3 T magnetic field (B) along the ring side (Fig. 1a), show a ferromagnetic "onion" state generating a magnetic dipole oriented along the square diagonal [1]. Upon reversing B, the magnetic dipole is reversed (Fig. 1b). With TEM Lorentz microscopy, by exploiting the objective lens magnetic field, a variable B (~ few mT) was applied along the ring side by varying the sample tilt. The overfocussed Fresnel image (Fig. 2a) shows bright and dark fringes along each side, typical of ferromagnetic nanowires [2]. Fringe contrast is continuous for three of the four sides, indicating a uniform magnetization of the nanowires. However, on the bottom-left side a discontinuity with contrast exchange is evident, indicating the presence of a domain wall. By increasing the tilt angle (Fig. 2b), i.e. by increasing B along that side, the domain wall position can be varied and controlled.

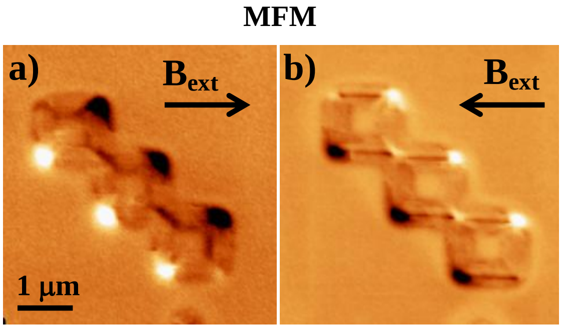

Fig. 1: MFM images of three Co square rings after applying a 0.3 T field (a) along ring side and (b) in opposite direction.

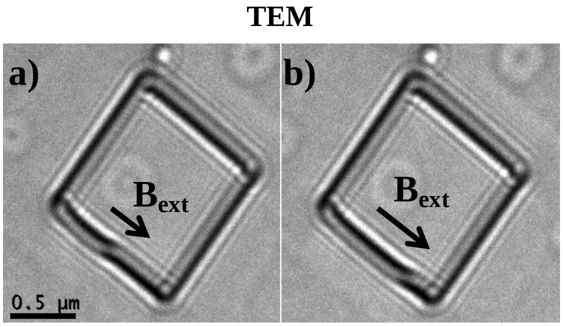

Fig. 2: Overfocussed TEM images of a Co ring taken at increasing tilt angle in order to increase the objective lens field along the side.

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FEBID of Fe and Co nanopillars - A versatile approach for high aspect ratio and low momentum magnetic tips for magnetic force microscopy

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The use of iron, nickel and cobalt precursors has provided focused electron beam induced deposition (FEBID) the capability of fabricating magnetic nanostructures [1]. With this 3-dimensional direct-write technique magnetic systems down to the nanoscale level have been realized [2]. Especially the fabrication of magnetic devices for nanomagneto logic (NML) applications has been focus of research efforts [3]. For magnetic investigation of such small nanostructures often magnetic force microscopy (MFM) has been preferred because of its non-invasiveness and its high resolution. Recent NML designs have also featured out-of-plane nanomagnets, such as perpendicular nanopillars, which has confronted the magnetic characterization of such high-aspect structures with a new challenge.

In this work we present high-aspect ratio MFM tips that are capable to characterize both in-plane and out-of-plane magnetic nanostructures of NML gates. Metal carbonyl precursors of iron and cobalt were used to synthesize magnetic nanopillars on AFM tips. Such high-aspect-ratio MFM tips excel commercially available MFM probes with pyramidal shape in MFM investigation of 3-dimensional structures. Fe-based pillars have been successfully deposited with high growth rates (~ 110 nm/s) on commercial AFM tips. From measurements of colloidal gold nanoparticles the deconvolution of the tip geometry revealed a tip radius of 32 +/- 6 nm. EBID-modified MFM probes demonstrated the low magnetic interaction of the with the magnetic specimen than commercial low moment MFM probes. "Softer" magnetic probing bears less risk of unwanted sample reverse magnetisation.

Finally, by co-injection of iron and cobalt precursor we have fabricated a binary alloy tip of Fe/Co. TEM and STEM-EELS elemental investigation of a FeCo-nanopillar prove the capability of FEBID to produce nanostructures based on a bi-metallic system. STEM-EELS confirms the presence of both elements. However, the Fe and Co distribution in the nanopillar appears not to be evenly distributed, but rather indicate a core shell nanostructure (Fig. 2).

The FEBID-tailored Fe and Fe/Co tips were used for magnetic characterisation of magnetic structures. The advantages and the limitations will be described and future application areas will be discussed.

We thank the CELINA COST- action for financial support of this work.

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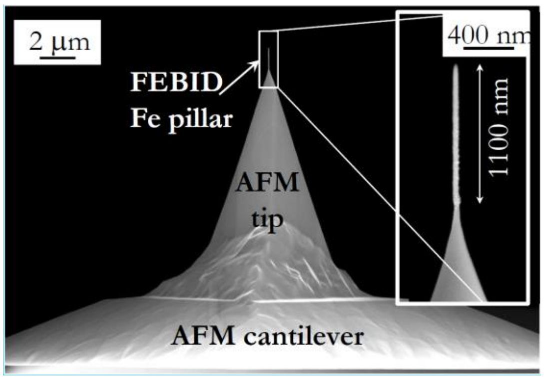

Fig. 1 SEM image of FEBID tip deposited from iron carbonyl on the AFM tip on a cantilever.

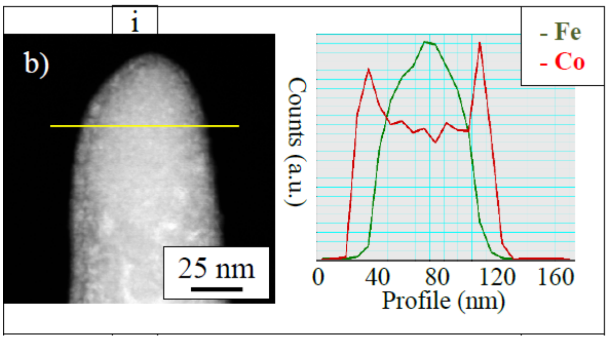

Fig. 2 TEM bright field image and STEM-EELS of a Fe/Co nanopillar deposited by FEBID of iron carbonyl and cobalt carbonyl using an exposure time of 5 s.

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