DS 23: Lithography II: Focused Electron Beam Induced Processing: 3D Nano-Printing for Material Science (Focussed Session): Afternoon Session (joint session DS/KFM)

Considering 3D printing using fused-deposition modeling or higher-resolution variants with lasers applicable to polymers and metals, an analogous approach exists on the nanometer scale. With the aid of focused electron beam-induced deposition (FEBID) it is possible to create solid-state structures on the nanoscale. However, in contradistinction to large-scale 3D printing of simple plastic or metallic structures, FEBID is able to directly provide nano-materials with a wealth of interesting electronic, optical and magnetic properties. Due to this, focused electron beam-induced deposition has experienced a rapid expansion in the breadth of its application fields over the last 10 years. FEBID uses precursor gases which, being adsorbed on a surface, are dissociated in the focussed electron beam to form the deposit. Intensive research has pushed the capabilities of FEBID in two important areas. It is now possible to obtain fully metallic nanostructures of Fe, Co and FeCo-alloys and also of Au and Pt. In addition, very recently the simulation-guided nano-manufacturing of 3D structures has matured to such a degree that even complex 3D objects can now be fabricated under controlled conditions. The focused session will address these new developments spanning the range from the fundamentals of electron-precursor interaction, covering aspects of the rational design of optimized precursors, and showing recent work on superconducting, magnetic and plasmonically active materials, both in 2D and 3D.

Organized by

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Time: Wednesday 15:00–18:00 Location: H 2032

DS 23.1 Wed 15:00 H 2032

FEBIP on Metal-Organic Frameworks — •Christian Preischl[1], Elif Bilgilisoy[1], Florian Vollnhals[1], Kai Ahlenhof[2], Petra Swiderek[2], Hartmut Gliemann[3], Christof Wöll[3], and Hubertus Marbach[1] — [1]Physik. Chemie II, FAU Erlangen — [2]IAPC, Universität Bremen — [3]Institut f. funktionelle Grenzflächen, KIT

We report the fabrication of nanostructures down to single digit nanometer scale on metal-organic frameworks (MOFs) by FEBIP. Next to EBID[1], our second technique is Electron Beam Induced Surface Activation (EBISA). In EBISA the surface is locally activated by an electron beam and the subsequently dosed precursor is catalytically decomposed at the activated sites and forms a deposit.[2] Both approaches were investigated with $Fe(CO)_5$ and $Co(CO)_3NO$ on HKUST-1 and Cu-oxalate which is somewhat similar to HKUST-1 but the benzylic part in the organic linker is missing compared to the latter. Both samples were grown in a layer-by-layer method.[3][4] We demonstrate that both precursors are suitable for EBID on both samples, whereas EBISA works only with $Fe(CO)_5$ on the HKUST-1. We will compare the corresponding results and discuss especially the high potential of MOFs as substrates for novel FEBIP processes towards the fabrication 3D materials.

[1] W. van Dorp, C.W. Hagen, J. Appl. Phys. 104 (2008), 081301 [2] H. Marbach, Appl. Phys. A 117 (2014), 987; Drost et al., Small Methods 1 (2017), 1700095 [3] O. Shekhah et al., Angew. Chem. Int. Ed. 48 (2009), 5038 [4] I. Schrader et al., Langmuir 30 (2014), 11945

DS 23.2 Wed 15:15 H 2032

Focused Electron Beam Induced Deposition with halogenated organometallic Ru compounds — •Jakub Jurczyk[1,2], Christopher Brewer[3], Olivia Hawkins[3], Czeslaw Kapusta[2], Lisa McElwee-White[3], and Ivo Utke[1] — [1]Empa - Swiss Federal Laboratories for Materials Science and Technology,Thun, Switzerland — [2]AGH University of Science and Technology in Krakow, Kraków, Poland — [3]University of Florida, Gainesville, USA

Focused Electron Beam Induced Deposition (FEBID) studies of potential organometallic halogenated ruthenium precursors were performed. By now the best Ru FEBID result was achieved using bis(ethylcyclopentyldienyl) ruthenium(II) [1] giving a C:Ru ratio of 9:1 (10 at.% Ru) in as deposited material. Recent gas phase [2] and surface science studies [3] selected halogenated organometallic compounds as potential FEBID precursors. In this contribution we present three of them: n-allyl-Ru(CO)3Cl, n-allyl-Ru(CO)3Br, n-allyl-Ru(CO)3I. The deposit metal content was investigated as function of growth regimes and writing strategies for vertical and planar structures. First promising results of up to 20 at.% of Ru in as deposited material were achieved. Electrical properties of as deposited and annealed nanowires will be presented.

[1] J.H. Noh et al., App. Phys. A, 117, (2014), 1705-1713 [2] R. M. Thorman et al., Phys. Chem. Chem. Phys, 19, (2017), 13264-13271 [3] Spencer et al., J. Phys. Chem. C, 119, (2015), 15349-15359

DS 23.3 Wed 15:30 H 2032

Electron-induced reactions of surface-grown metal organic layers — •Kai Ahlenhoff and Petra Swiderek — University of Bremen, Institute for Applied and Physical Chemistry, Bremen, Germany

Metal-containing coordination materials grown on surfaces using layer-by-layer self-assembly processes are advantageous for focused electron beam deposition (FEBID) processes for several reasons. First, multilayer materials can serve as precursors which enable high processing speed due to their large surface density [1]. Also, an adlayer on a substrate used in a regular FEBID process relying on volatile precursors can suppress secondary electron emission from the underlying solid and thus lead to more precisely defined deposit shapes [2]. Third, the layer may be activated by an electron beam to provide a template for area-selective autocatalytic deposit growth in an EBISA process [2].

Despite these advantages, little is known about the electron-induced reactions in such materials and the resulting products. Therefore, this contribution presents studies on electron-induced desorption (ESD) from and post-irradiation reflection absorption infrared spectroscopy (RAIRS) of several surface grown metal-organic coordination polymers such as copper(II)oxalate [3] and HKUST-1 [4] but also including novel FEBID precursors.

References: [1] M. Bresin et al. Nanotechnol. 24 (2013) 035301. [2] M. Drost et al., SMALL Methods 1 (2017) 1700095. [3] K. Rückriem et al., Beilstein J. Nanotechnol. 7 (2016) 852. [4] B.W. Jacobs et al., Nanotechnol. 22 (2011) 375601.

DS 23.4 Wed 15:45 H 2032

Tuning and in-situ monitoring the hall resistance of ferromagnetic FEBID structures — •Roland Sachser and Michael Huth — Physikalisches Institut, Goethe-University, Frankfurt am Main, Germany

$HFeCo_3(CO)_{12}$ is an excellent FEBID precursor, which allows the deposition of magnetic and metallic CoFe alloy nanostructures. In contrast, the widely used $(CH_3)_3CH_3C_5H_4Pt$ standard precursor results in insulating deposits, consisting of Pt nanograins embedded in a carbonaceous matrix. In this contribution we will present measurements on samples prepared via co-deposition of both precursors. Varying the deposition conditions, the metal content of the deposits, and thus, the resistivity and the Hall resistance of the samples can be tuned. Furthermore, the co-deposited samples are sensitive to post-growth electron beam irradiation, which influences its electrical transport properties, as it is already known for normal FEBID deposits obtained by the Pt-precursor. We will show in-situ measurements of the Hall resistance directly inside the SEM by using the magnetic field provided by the immersion lens of the instrument. Further characterization is done via temperature-dependent electrical and magnetotransport measurements.

DS 23.5 Wed 16:00 H 2032

Purified and crystalline three-dimensional electron-beam-induced deposits: the successful case of cobalt — Javier Pablo-Navarro[1], César Magén[1,2], and •José María De Teresa[1,2] — [1]Laboratorio de Microscopías Avanzadas (LMA) - Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain. — [2]Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain.

Purified and crystalline 3D cobalt nanowires of diameter below 90 nm have been fabricated by ex-situ high-vacuum annealing at 600 Celsius degrees after FEBID growth. While increasing the metallic content of the nanowires up to 95 atomic percent, the thermal annealing process induces the recrystallization of the pseudo-amorphous as-grown structure into bulk-like, hcp and fcc crystallites with lateral sizes comparable to the width of the nanowire. The net magnetization increases 80 percent with respect to as-grown values, close to the bulk cobalt value. This achievement opens new pathways for applications of this synthetic method in the fabrication of either individual or arrays of 3D high-purity and crystalline cobalt nanowires for high-density memory and logic devices, nanosensors and actuators, and could be a viable method to obtain other pure and crystalline 3D materials by FEBID.

DS 23.6 Wed 16:15 H 2032

Exploring new copper complexes for FEBID — •Luisa Berger[1], Katarzyna Madajska[2], Nils Boysen[3], Iwona Barbara Szymánska[2], Anjana Devi[3], and Ivo Utke[1] — [1]Empa - Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland — [2]Nicolaus Copernicus University, Torun, Poland — [3]Ruhr-Universität Bochum, Germany

Focused electron beam induced deposition (FEBID) is a well-established maskless direct write method for nanostructures [1]. The deposition of pure copper with FEBID has not been achieved so far and metal contents typically reached 13-25 at.% [2]. By exploring novel copper precursor classes - fluorinated copper carboxylates ([Cu2(u-O2CCF2F5)4], [Cu2(EtNH2)2(u-O2CCF2F5)4]) and a fluorine-free β-diketonate (Cu(tbaoac)2) - we intend to achieve the deposition of high purity structures. The latter was employed in FEBID recently [3] while carboxylates were reported as CVD precursors [4]. The influence of varying deposition parameters on appearance and composition was investigated. First interesting results lead to copper contents of 25 at.%.

[1] I. Utke, A. Gölzhäuser, Angew. Chem. Int. Ed. 49 (2010), 9328.
[2] A. Luisier et al., Journal of The Electrochemical Society, 151 (2004) C535.
[3] C. Haverkamp, K. Höflich et al., Beilstein Journal of Nanotechnology 2017 (in review)
[4] P. Piszczek, I. B. Szymańska, Chem. Vap. Deposition, 19 (2013) 251.

15 min. break.

DS 23.7 Wed 16:45 H 2032

Dedicated AS-ALD micro-reactor for FEBID nano-templates — •Peter Gruszka, Giorgia Di Prima, Roland Sachser, and Michael Huth — Goethe Universität, Max-von-Laue-Str. 1, 60438 Frankfurt am Main, Germany

In recent years, conventional methods of nano-structuring are slowly reaching their lower limits. A novel bottom-up approach emerged[1], which combines focused electron beam induced deposition(FEBID) and area-selective atomic layer deposition(AS-ALD). FEBID is a serial, bottom-up and direct-write technique yielding structures with superior lateral resolution ($<$ 10 nm), but with poor material quality. In contrast, ALD and especially AS-ALD are parallel and bottom-up approaches with exceptional thickness control resulting in high purity sub-nano films.

We successfully performed the combined FEBID-ALD process in our Nova 600 Dual Beam scanning electron microscope.[2] The ALD experiments were conducted on purified platinum FEBID-nanostructures[3] which were monitored via in-situ conductance measurements. For further investigation and optimization, we built a dedicated AS-ALD micro-reactor.

[1] Mackus, et al., J. Appl. Phys 107 (2010), 116102
[2] Di Prima, et al., Nano Futures 1(2) (2017), 25005
[3] Sachser, et al., ACS Appl. Mater. Interfaces 6 (2014), 15868

DS 23.8 Wed 17:00 H 2032

Fabrication of multi-component nanostructures by FEBID — •Fabrizio Porrati[1], Roland Sachser[1], Sven Barth[2], Gian Carlo Gazzadi[3], Stefano Frabboni[3], Christian Gspan[4], Harald Plank[4], Andreas Terfort[5], and Michael Huth[1] — [1]Goethe-Universität, Institut of Physics, Frankfurt am Main, Germany — [2]TU Vienna, Institute of Materials Chemistry, Wien, Austria — [3]University of Modena and Reggio Emilia, FIM Department, Modena, Italy — [4]TU Graz, Institute for Electron Microscopy and Nanoanalysis, Graz, Austria — [5]Goethe-Universität,Institute for Inorganic and Analytical Chemistry, Frankfurt am Main, Germany

The fabrication of multi-component polycrystalline or granular metals by FEBID represents a challenging research approach for the design of novel nanostructured materials. Currently, there are three different approaches for the fabrication of multi-component FEBID nanostructures: 1. deposition by single source heteronuclear precursors; 2. codeposition using two different precursors; 3. intermixing of multilayer nanostructures fabricated with different precursors by low-energy electron irradiation. These fabrication approaches allow the fabrication of a large number of tunable alloy nanostructured and intermetallic compounds. In this contribution, we present some examples of binary and ternary nanostructures fabricated by following these routes. In particular, we report on the fabrication, the structural characterization and magnetotransport measurements of CoFe alloys and Co2FeSi Heusler compounds.

DS 23.9 Wed 17:15 H 2032

Ac response of nano-granular metals prepared via FEBID — •Marc Hanefeld and Michael Huth — Physikalisches Institut, Goethe Universität, Max-von-Laue-Str. 1, 60438 Frankfurt am Main, Germany

Granular metals are of great interest for material sciences due to their diverse electronic transport properties and can generally be described as metallic nanoparticles surrounded by a dielectric amorphous matrix. They show promising possibilities for applications in different sensing mechanisms [1] and pose a topic of ongoing research concerning their response to a time-dependant ac stimulus [2].

Focused Electron Beam Induced Deposition (FEBID) is a versatile technique to create nano-granular metals comprising a variety of elements and a high tunability of the samples properties. Additionally, electron irradiation is the perfect tool to tune important conduction parameters like the inter-grain coupling strength and the volume fraction of the crystallites compared to the surrounding matrix, ultimately influencing the conductance regime of the deposits. In our group we have a wide knowledge about Pt(C)-FEBID deposits and the effect of electron irradiation upon them, as well as their dc electronic transport properties [1]. We will present first measurements on the ac response of such deposits and show the capabilities of FEBID to create an ideal model environment for an in depth analysis of the ac conduction characteristics of granular metals depending on their properties.

[1] Huth, et al., Microelect. Eng. 2017. doi:10.1016/j.mee.2017.10.012.
[2] Bakkali, et al., Sci. Rep. 2016;6:29676. doi:10.1038/srep29676.

DS 23.10 Wed 17:30 H 2032

Energy collection from green-house infra-red emission using nanogranular compoundmaterials — •Koops Hans Wilfried

Peter — HaWilKo GmbH , Ober-Ramstadt, Germany

According to a 10 years average measurement of NASA of the earth's energy household, the sun sends 340,4 W/m^2 direct to the earth, but only 163,3 W/m^2 reach the ground. In the IR a backreflection from greenhouse gases delivers 340 W/m^2.

A nanogranular Pt/C material has a bandgap of 128 meV, which allows to absorb IR-Light. This radiation can be absorbed by a nanocrystalline Pt/C compound. Large absorber areas can be used. Silicon material absorbes only energies above 1.3 eV during daylight from the visible light. The green house gases, however, emit their radiation all day and night in the IR. The absorbed IR photons can be stored in the compound material as coherent Boson fields. A field gradient applied to such fields can move the Bosons and make them decay at the end of the field, and release electrons as a current. HaWilKo can produce a 1 cm^2 large sheet to demonstrate the energy harvesting in the IR.

DS 23.11 Wed 17:45 H 2032

Coordination compounds for focused electron beam induced deposition (FEBID) — •Iwona Szymańska. and Katarzyna Madajska — Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland

Focused electron beam induced deposition is a direct maskless nanolithography technique. The compounds applied as FEBID precursors should effectively generate volatile metal carriers, which are transported over a substrate. Next, they are irradiated by high-energy electrons and decompose forming nanomaterials [1]. Copper and silver exhibit high electrical and thermal conductivity and are extensively used in microelectronics.

Copper and silver carboxylate compounds were applied as CVD precursors [2,3]. Carboxylates are able to coordinate as monodentates, chelates, and bridges forming complexes of diverse nuclearity. Secondary ligands enable manipulating physicochemical parameters of precursors. Research was focused on the copper(II) and silver(I) carboxylate compounds, which seems to be promising for a FEBID process. The usefulness of a thermal analysis, EI MS spectrometry, and VT IR spectroscopy for the FEBID precursors selection was evaluated. The secondary ligand influence was studied basing on primary amines.
Acknowledgements: The authors wish to thank Nicolaus Copernicus University in Toruń (Statute Research no.103) for a financial support.

References: [1] I. Utke et al., Angewandte Chemie Int. Ed., 49 (2010) 9328; [2] A. Grodzicki et al., Coord. Chem. Rev., 249 (2005) 2232; [3] I.B. Szymańska„ Polyhedron, 65 (2013) 82.