TT 48: Focus Session: Direct-Write Nanofabrication and Applications II (Electron Beam Induced Processing) (joint session DS/TT)

Part II: New Approaches & Chemsitry

Organizers:

• Michael Huth, Physikalisches Institut, Goethe-Universität, Frankfurt, Germany

• Harald Plank, FELMI-ZFE, TU Graz, Austria

(Synopsis provided with part I of this session)

Time: Wednesday 15:00–18:00 Location: H32

Invited Talk TT 48.1 Wed 15:00 H32

Fabrication of functional nanostructures by electron and ion beams — •Milos Toth — University of Technology Sydney, Australia

Focused electron and ion beams can be used to restructure/mill materials and initiate surface reactions supplied by gas-phase precursor molecules. The chemical reactions give rise to processes that fall into two broad categories: direct-write lithography and emergent phenomena. The latter include topographic surface patterns defined by the crystal symmetry of the sample and chemical structure of a precursor gas, and self-assembly of complex 3D nanostructures. Here I will review the underlying mechanisms, and applications of the techniques to materials used in optoelectronics, plasmonics and quantum photonics. Specific applications include the fabrication and iterative editing/tuning of plasmonic nanostructures and dielectric optical cavities, site-selective electron beam induced fluorination of surfaces, fabrication of isolated colour centres that act as on-demand single-photon-emitters in 2D hBN, and dynamic SEM studies of the degradation of phosphorene in which an electron beam is used to simultaneously initiate chemical reactions and to image propagating reaction fronts. These applications demonstrate the benefits and shortcomings of ion beam and electron beam techniques in terms resolution, throughput and damage imparted to functional materials by beams comprised of electrons, and Ga, Xe, O and He ions.

TT 48.2 Wed 15:30 H32

Avoiding amorphization in silicon nano structures — •Gregor Hlawacek[1], Xiaomo Xu[1,2], Hans-Jürgen Engelmann[1], Karl-Heinz Heinig[1], Wolfhard Möller[1], Ahmed Gharbi[3], Raluca Tiron[3], Lothar Bischoff[1], Thomas Prüfer[1], Rene Hübner[1], Stefan Facsko[1], and Johannes von Borany[1] — [1]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany — [2]Faculty of Physics, Technische Universität Dresden, Dresden, Germany — [3]CEA-Leti, Grenoble, France

The usage of ion beam irradiation on vertical nanopillar structures is a prerequisite for fabricating a vertical GAA-SET device. After room temperature irradiation (2×10^{16} ions/cm^2) of nanopillars (with a diameter of 35 nm-50 nm and a height of 70 nm) with either 50 keV broad beam Si^+ or 25 keV focused Ne^+ from a helium ion microscope (HIM), strong plastic deformation has been observed which hinders further device integration. This differs from predictions made by Monte-Carlo based simulations using the program TRI3DYN. To avoid this, ion irradiation at elevated temperatures (up to 672 K) has been performed and no plastic deformation was observed under these conditions. Additionally a pillar diameter reduction by 50% can ab achieved in this way without changing the shape of the pillar.

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TT 48.3 Wed 15:45 H32

Non-classical Liquid Metal Ion Sources for advanced FIB nano-patterning — •Paul Mazarov[1], Lothar Bischoff[2], Wolfgang Pilz[2], Nico Klingner[2], Achim Nadzeyka[1], Jorg Stodolka[1], and Jacques Gierak[3] — [1]Raith GmbH, Konrad-Adenauer-Allee 8, 44263 Dortmund, Germany — [2]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Bautzner Landstrasse 400, 01328 Dresden, Germany — [3]LPN-CNRS, Route de Nozay, 91460 Marcoussis, France

Focused Ion Beam (FIB) processing has been developed into a well-established and still promising technique for direct patterning and proto-typing on the nm scale. Exploring the Liquid Metal Alloy Ion Sources (LMAIS) potential represents a promising alternative to expand the global FIB application fields. Especially, ion beam nanofabrication as direct, resistless and three-dimensional patterning enables a simultaneous in-situ process control by cross-sectioning and inspection. Thanks to this, nearly half of the elements of the periodic table are made available in the FIB technology as a result of continuous research in this area during the last forty years. Recent developments could make these sources to an alternative technology feasible for nanopatterning challenges. In this contribution the operation principle, the preparation and testing process as well as prospective domains for modern FIB applications will be presented. As an example we will introduce a Ga35Bi60Li5 LMAIS in detail. It enables high resolution imaging with light Li ions and sample modification with Ga or heavy polyatomic Bi clusters, all coming from one ion source.

TT 48.4 Wed 16:00 H32

Opening the Door to New Beam Induced Processing Applications: A Compact and Flexible Gas Injection System — •Andrew Jonathan Smith, Klaus Schock, Andreas Rummel, and Stephan Kleindiek — Kleindiek Nanotechnik, Aspenhaustr. 25, 72770 Reutlingen, Deutschland

A flexible GIS module that can be filled with precursor material by the user is introduced. This module is comprised of a small temperature controlled reservoir, a nozzle, and a motor that actuates a valve. Using a micromanipulator, it is possible to position the GIS nozzle precisely while being able to move it far away from the sample so that it is not an obstacle during other processing/imaging steps.

The reservoir can be loaded with solid or liquid precursor materials. It is also possible to feed gaseous precursors from a source outside of the microscope's vacuum chamber. The gas is then introduced using a precisely controllable needle valve.

This approach allows for a high degree of flexibility in choosing precursor materials. Switching precursors is as simple as exchanging the plug-in module on the MM3A-EM micromanipulator. Also, utilizing multiple GI-Systems for specialized tasks is made easy and cost effective.

Having a compact and flexible GIS that can be loaded with virtually any precursor ma- terial provides a multitude of possibilities for exploring novel solutions to existing problems as well as new applications for beam induced deposition processes.

TT 48.5 Wed 16:15 H32

FXBID - an X-ray based sibling to FEBIP — •Andreas Späth[1], Kim Thomann[1], Florian Vollnhals[1], Jörg Raabe[2], Kevin C. Prince[3], Robert Richter[3], Wolfgang Hieringer[4], Hubertus Marbach[1], and Rainer H. Fink[1] — [1]Physikalische Chemie II, FAU Erlangen-Nürnberg, Germany — [2]Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland — [3]Elettra Sincrotrone, Basovizza, Italy — [4]Theoretische Chemie, FAU Erlangen-Nürnberg, Germany

Focused X-ray beam induced deposition (FXBID) is a novel technique for the additive fabrication of metallic nanostructures by illuminating metal organic precursor molecules with focused soft X-rays in a Fresnel zone plate based scanning transmission X-ray microscope (STXM)[1,2]. An advantage of the technique is the possibility to optimize precursor fragmentation by proper selection of the incident photon energy. For a better understanding of basic X-ray induced fragmentation processes, we have performed photon energy dependent mass spectrometry and secondary electron spectroscopy studies for several metal organic precursors[3]. The results are correlated with TD-DFT calculations of the molecular orbitals relevant for soft X-ray absorption and have been transferred to advanced deposition experiments. We have started to explore the capabilities of in-situ cleaning procedures (reactive gases, annealing, etc.) to enhance the chemical purity of FXBID deposits. The project is funded by DFG grant SP 1775/1-1.

[1] A. Späth et al., RSC Advances, 2016, 6, 98344.
[2] F. Tu et al., J. Vac. Sci. Technol. B, 2017, 35(3), 031601.
[3] A. Späth et al., Microsc. Microanal. 2018, 24(S2), 114.

15 min. break

Invited Talk TT 48.6 Wed 16:45 H32

Fundamentals of low-energy electron induced dissociation of focused electron beam induced deposition precursors — •Oddur Ingólfsson — Science Institute and the Department of Chemistry, University of Iceland,, Dunhagi 3, 107 Reykjavík. Iceland.

When high-energy electron beams imping on a solid surface, as is the case in FEBID, backscattered and secondary electrons (SEs) are abundant. The energy distribution of the SEs typically peaks well below 10 eV, has a significant contribution close to 0 eV and a tail to higher energies. In this energy range, electron induced bond ruptures through Dissociative Ionization, Dissociative Electron Attachment and Neutral and Dipolar Dissociation can be very efficient. These processes have different energy dependence and the nature and thus the reactivity of the fragments formed is also distinctly different. The cross sections for these processes and the branching ratios for different dissociation paths depend critically on the respective molecular composition. This, in turn opens opportunities to tailor the sensitivity of potential FEBID precursors towards preferred paths to achieve better deposition efficiency and better composition control. In this contribution fundamental aspect of electron induced dissociation processes are discussed in context to their role in FEBID. Acknowledgement; This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722149.

TT 48.7 Wed 17:15 H32

Which molecular structures in metal organic compounds are favourable for electron-induced decomposition? — Kai Ahlenhoff and •Petra Swiderek — University of Bremen, Institute for Applied and Physical Chemistry, Bremen, Germany

Electron beam induced processing calls for precursor molecules or materials that can be converted to a deposit with well-defined final composition. An approach to this problem is to use ligands which fragment to non-reactive and volatile products leaving behind only the desired material. This concept can guide the design of precursor materials. We have started to investigate this hypothesis by comparing the electron-induced decomposition of surface-grown copper-containing coordination materials that are constructed using different organic counterions, namely, copper(II)oxalate, copper(II)squarate, and HKUST-1 [1]. As a second class of compounds, silver carboxylates with different organic side chain have been considered. Using these examples, we discuss in this contribution a new concept for precursor design. [1] K. Ahlenhoff et al., Phys. Chem. Chem. Phys., submitted.

TT 48.8 Wed 17:30 H32

Cisplatin as potential Pt FEBID precursor: NH_3 ligands enhance the electron-induced removal of chlorine — •Markus Rohdenburg[1], Kai Ahlenhoff[1], Sascha Koch[2], Armin Gölzhäuser[2], and Petra Swiderek[1] — [1]Institute for Applied and Physical Chemistry, University of Bremen, Leobener Str. 5, 28359 Bremen, Germany — [2]Department of Physics, University of Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany

As recently shown, electron beam exposure to crystals of cisplatin (cis-$Pt(NH_3)_2Cl_2$) leads to a violent reaction. The crystal literally boils with a deposit of pure Pt remaining behind [1]. We have proposed that this reaction is driven by the electron-induced fragmentation of the NH_3 ligands which supplies hydrogen that converts chlorine ligands into HCl. In contrast, the structurally similar cis-$Pt(CO)_2Cl_2$ rapidly loses CO upon irradiation but yields deposits with high chlorine contents that can only be removed by extensive electron exposure [2]. We therefore present new results that confirm the formation of HCl by use of electron-stimulated desorption (ESD) experiments. Furthermore, XPS data reveals that electron irradiation removes N and Cl from cisplatin on a similar time scale. The exposure required for quantitative removal of Cl is much smaller in the case of cisplatin than for cis-$Pt(CO)_2Cl_2$ underlining the favourable effect of the NH_3 ligands.

[1] J. Warneke et al., J. Phys. Chem. C 120 (2016) 4112.
[2] J.A. Spencer et al., J. Am. Chem. Soc. 138 (2016) 9172.

TT 48.9 Wed 17:45 H32

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

Focused electron beam induced deposition (FEBID) is said to play a fundamental role for making sophisticated 2D and 3D nanostructures with an ultimate resolution of less than 1 nm. It is frequently so-called *3D nanoprinting*.[1] The choice of the precursor is crucial for the success of FEBID: its chemical nature and dissociation behavior determine the composition of the deposit.[2]

Research was focused on the copper(II), silver(I) and rhenium(III) complexes with an amidinate and/or carboxylate ligands, which seems to be promising for a FEBID process. Mass spectrometry (EI MS) exhibited in the gas phase following ions: [Cux(NH2(NH=)CR1)y(O2CR2)z]+, [Agx(NH(NH=)CR1)y(O2CR2)z]+, [Agz(NH(NH=)CR1)y]+, [Re2Clx(NH(NH=)CR1)y], where R1, R2 = perfluorinated aliphatic groups. Sublimation experiments and temperature-variable infrared spectroscopy were carried out to determine compounds volatility and decomposition mechanisms.

References [1] D. Belić, M. M. Shawrav, E. Bertagnolli, H. D. Wanzenboeck, Beilnstein J. Nanotechnol, 8 (2017) 2530*2543. [2] I. Utke, P. Hoffmann, J. Melngailis, J. Vac. Sci. Technol. B, 26 (2008) 1197*1276.