Direct Nanoprototyping of Functional Materials via Focused Electron Beam

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Doctoral Thesis
2013

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Anastasia Riazanova:  
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Akademisk avhandling som med tillstånd av Kungl Tekniska Högskolan framlägges till offentlig granskning för avläggande av teknologie doktorsexamen i materialvetenskap fredagen den 15 november 2013 klockan 10:00 i sal F3, Lindstedtsvägen 26, Kungl Tekniska Högskolan, SE-100 44 Stockholm.

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ABSTRACT

During recent years the demand for nanoscale materials with tailor-made functional properties as bulk species, is continuously and progressively rising for such fields as e.g. micro- and nano-electronics, plasmonics, spintronics, bio-technology, bio-sensing and life sciences. Preserving and / or improving properties of functional materials with their simultaneous size reduction and high-resolution site-specific positioning is indeed very challenging, for both conductors and insulators.

One of the advanced nanoprototyping methods that can be utilized for this purpose is the Electron-Beam-Induced Deposition, or shortly EBID. This process is based on a local decomposition by a focused electron beam of a precursor gas molecules adsorbed on the sample’s surface. The beauty of this method is that it gives a unique possibility of rapid creation of site-specific nanoscale 3D structures of precise shape in a single operation. It’s an additive process that can be easily combined with other patterns.

However, besides all the benefits, EBID has some constraints, in particular low purity of the deposited materials, due to the organometallic nature of the used precursors. Chemical composition of EBID patterns is strongly dependent on the chosen gas chemistry, the substrate, many deposition parameters and post-treatment processes applied to the deposited structures.

In our research we focused on deposition of Co, Au, SiO$_2$, C, W and Pt, their purification and shape control. And this thesis presents an overview of our accomplishments in this field.

Depending on the gas chemistry of interest, three major purification approaches of EBID-grown materials were tested out:

✓ Post-deposition annealing: in air and in the controlled atmosphere,
✓ Deposition onto a preheated substrate,
✓ Deposition in the presence of reactive gases.

As a result, a dramatic purity improvement was observed and a significant advancement was achieved in creation of high-purity gold, cobalt and silicon dioxide nanoscale structures. In particular:

1) For the Me$_2$Au(acac) precursor, we developed a nanofabrication routine combining application of wetting buffer layers, fine tuning of EBID parameters and subsequent post-annealing step, which led to formation of high-purity planar and high aspect ratio periodic Au nanopatterns. We also describe the adopted and gently adjusted wet etching method of undesirable buffer layer removal, required in some cases for the further device application.

2) For the Co$_2$(CO)$_8$ precursor, in-situ seeded growth in conjunction with EBID at the elevated substrate temperature resulted in a deposition of pure nanocrystalline Co with magnetic and transport properties close to the bulk material.

3) For the tetraethyl orthosilicate precursor, or shortly TEOS, assisting of the deposition process with the additional oxygen supply led to the EBID of carbon-free amorphous insulating Si-oxide, with the absorption and refraction properties comparable to those for fused silica.

Several applications of EBID nanopatterns are also discussed.

**Keywords:** EBID, nanoprototyping, nanopatterning, nanoscale, nanostructure, purification, Au, Co, SiO$_2$, dimethyl gold acetylacetonate, dicobalt octacarbonyl, TEOS, Dual Beam.
ACKNOWLEDGEMENTS

Dedicated to my dear mom, Iryna Riazanova

“Learning is the eye of mind!”

A. V. Suvorov

When four and half years ago I was stepping onto the challenging pathway of my doctoral studies at Royal Institute of Technology, I had not even been thinking about how memorable and significant this period would turn up for me, or how many discoveries it would lead to and how much it would facilitate my development, both in the area of science and research, and in various personal aspects. Now, being really close to my defense and realizing how much I grew up, I would like to sincerely acknowledge the following people to whom, I think, I owe all these achievements.

First of all I would like to express endless gratitude to my principal supervisor Prof. Lyuba Belova for believing in me and giving me a great opportunity to become a part of her research group. Dear Lyuba, thank you so much for introducing me to the state-of-the-art microscopy world and for teaching me so enthusiastically. I truly appreciate your infinite care and your devoted parental support, and I owe you majority of the skills that I mastered in the nanofabrication area. Now, thanks to you I am feeling myself as “a creative nanoscale artist” with almost unlimited capabilities for the design of materials of the future.

Throughout the past years, my PhD studies would be nothing without dedicated support of my co-supervisors: Dr. Hans Mulders (FEI Electron Optics, The Netherlands) and Prof. K. V. Rao. Your valuable advices and wise mentoring significantly helped me understand the essence of my scientific project and develop as researcher.

One more very special person, to whom I am infinitely grateful, is Prof. E. Dan Dahlberg from University of Minnesota, USA. Dear Dan, I would like to heartily thank you for every single discussion that we had and for all the time you spent with me. Your dedicated attention played one of the key roles in my doctoral education.

As well, I would like to express my deep gratitude to Prof. Börje Johansson for his continuous support during my PhD studies at KTH.
I would like to give sincere thanks to Piet Trompenaars (FEI Electron Optics, The Netherlands) and Dr. Valter Ström for their dedicated help throughout the whole experimental process of our scientific projects. Your highly respected comments and novel solutions in this research area considerably facilitated the quality and the progress of my PhD work.

I am very grateful to Yuri Rikers (FEI Electron Optics, The Netherlands) for all the help with high-end TEM characterization. I would like to thank Prof. Andrei Kabashin and Dr. Andrey Aristov from Aix Marseille University for the superb optical studies and sharing their expertise and experience. I truly appreciate the enthusiastic assistance of Barry Nicholas Costanzi (University of Minnesota, USA) with the electrical measurements of EBID samples.

I am very thankful to all my colleagues in our research group, in particular: Dr. M. Kapilashrami, Dr. F. Mei, Dr. A. Masood, Dr. Y. Wu, Dr. S. K. Mahadeva, Wolfgang Voit and Dr. S. Nagar. You made my work more cheerful and supported me in the lab when it was needed. I am very glad that I met you guys.

As well, I would like to gratefully acknowledge the Swedish Institute, the FEI Company (The Netherlands), the Swedish Research Council, the Swedish Foundation for Strategic Research and the Swedish funding agency VINNOVA for financial support, provided during my doctoral studies.

I am deeply obliged to the teachers, who were raising me up and were helping me to build up the fundamental knowledge, at the schools and the academy of PSACE&A in my hometown (Dnepropetrovsk, Ukraine) – without you I most probably would not be able to begin my PhD studies at KTH.

And the last, but definitely not least, I would like to heartily thank all my dear friends and my family for their great support and faith in me and my research. Thanks to you, I did not lose hope and went all the way through. Especially, I would like to express the deepest gratitude to my beloved mother – the person who was the first teacher in my life and who inspired me to start the scientific career.

Anastasia Riazanova
Stockholm, October 2013
SUPPLEMENTS

1. List of Papers and Manuscripts in the Thesis

**Supplement I:**
“Pattern shape control for heat treatment purification of electron-beam-induced deposition of gold from the Me$_2$Au(acac) precursor” *
Riazanova AV, Rikers YGM, Mulders J JL, Belova LM

**Supplement II:**
“Gas-assisted electron-beam-induced nanopatterning of high-quality Si-based insulator” *
Riazanova AV, Aristov A, Rikers YGM, Ström V, Mulders J JL, Kabashin AV, Belova LM

**Supplement III:**
“Creation of patterned gold nanostructures via electron-beam-induced deposition” *
Riazanova AV, Mulders J JL, Belova LM

**Supplement IV:**
“Electron beam induced deposition at elevated temperatures: compositional changes and purity improvement” **
Mulders J JL, Belova LM, Riazanova A
*Nanotechnology* 22, 055302 (2011).

**Supplement V:**
“Rapid electron beam assisted patterning of pure cobalt at elevated temperatures via seeded growth” **
Belova LM, Dahlberg ED, Riazanova A, Mulders J JL, Christophersen C, Eckert J
*Nanotechnology* 22, 145305 (2011).

**Contribution Statement of the Author:**
* Experiments, data analysis, literature survey and write up of the manuscript’s draft.
** Part of the experiments, data analysis, and participation in the manuscript’s write up.

2. List of the Conferences at which Parts of the Thesis Work Have Also Been Presented:

   *Poster presentation* “Electron- and Ion-Beam Induced Deposition of Gold Using Me$_2$Au(acac) Precursor and Purification Strategies”.

II. **International FIB/DualBeam UserClub Meeting**, 25-27 October 2010,

    “Electron Beam Induced Deposition – the Future of Advanced Nanoprototyping”.
IV. Euro AFM Forum 2011, 7-9 September 2011, Zurich, Switzerland.
Oral presentation “Direct E-Beam Writing and Its Implications for SPM Analysis”.
Poster presentation “Direct E-Beam Writing and Its Implications for SPM Analysis”. Participation in the image contest.

Oral presentation “Purity and Shape Control of Au EBID Structures”.

VI. 4-th Workshop on Focused Electron Beam Induced Processing (FEBIP 2012), 19-21 June 2012, Zaragoza, Spain.
Oral presentation “Purity and Shape Control of Au EBID Structures”.

VII. 2013 MRS Spring Meeting & Exhibit, 1-5 April 2013, San Francisco, California.
Poster presentation “Creation of Patterned Gold Nanostructures via Electron-Beam-Induced Deposition”.

3. List of Papers, Conference Proceedings and Manuscripts Not Included in the Thesis

I. “Enhanced photoresponse of inkjet printed ZnO thin films induced by chemically capped CdS nanoparticles by dip coating”
Wu Y, Tamaki T, Volotinen T, Riazanova A, Belova L, Rao KV

II. “Band gap engineering and room temperature ferromagnetism of Mg$_x$Zn$_{1-x}$O thin films”
Mahadeva SK, Quan Z, Fan JC, Albargi HB, Gehring GA, Riazanova AV, Belova LM, Rao KV

III. “Room temperature ferromagnetism and band gap engineering in Mg doped ZnO RF/DC sputtered films”
Mahadeva SK, Quan Z, Fan JC, Albargi HB, Gehring GA, Riazanova AV, Belova LM, Rao KV

IV. “Magnetic properties of inkjet printed Fe-doped ZnO thin films”
Fang M, Riazanova AV, Belova L, Rao KV
Submitted (2013).

V. “Magnetism of Fe-doped MgO thin films prepared by inkjet printing”
Fang M, Riazanova AV, Belova L, Rao KV
Submitted (2013).

VI. “Characterization of oxide films formed on Alloy 690 under simulated PWR primary water conditions”
Chen J, Öijerholm J, Lindberg F, Riazanova A, Bengtsson B
**NOMENCLATURE, ABBREVIATIONS AND DENOTATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AMR</td>
<td>anisotropic magneto-resistance</td>
</tr>
<tr>
<td>BF</td>
<td>bright field</td>
</tr>
<tr>
<td>BSE</td>
<td>backscattered electrons</td>
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<tr>
<td>CCD</td>
<td>charge-coupled device</td>
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<tr>
<td>CDEM</td>
<td>continuous dynode electron multiplier</td>
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<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>DA</td>
<td>dot array</td>
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<tr>
<td>DT</td>
<td>dwell time</td>
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<tr>
<td>EBID</td>
<td>electron-beam-induced deposition</td>
</tr>
<tr>
<td>EBSD</td>
<td>electron-backscattered detector</td>
</tr>
<tr>
<td>EDXS</td>
<td>energy-dispersive X-Ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy-loss spectroscopy</td>
</tr>
<tr>
<td>FEB</td>
<td>focused electron beam</td>
</tr>
<tr>
<td>FEG</td>
<td>field emission gun</td>
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<tr>
<td>FIB</td>
<td>focused ion beam</td>
</tr>
<tr>
<td>FMRFM</td>
<td>ferromagnetic resonance force microscopy</td>
</tr>
<tr>
<td>GIS</td>
<td>gas injection system</td>
</tr>
<tr>
<td>HAADF</td>
<td>high-angle annular dark-field</td>
</tr>
<tr>
<td>HAR</td>
<td>height to area ratio</td>
</tr>
<tr>
<td>HR</td>
<td>high-resolution</td>
</tr>
<tr>
<td>IBID</td>
<td>ion-beam-induced deposition</td>
</tr>
<tr>
<td>$k_\lambda$</td>
<td>absorption index</td>
</tr>
<tr>
<td>LMIS</td>
<td>liquid metal ion source</td>
</tr>
<tr>
<td>LN$_2$</td>
<td>liquid nitrogen</td>
</tr>
<tr>
<td>LOM</td>
<td>light optical microscope</td>
</tr>
<tr>
<td>MeCpPtMe$_3$</td>
<td>methyl cyclopentadienyl (trimethyl) platinum (IV)</td>
</tr>
<tr>
<td>MEMS</td>
<td>micro-electromechanical system</td>
</tr>
<tr>
<td>Me$_2$Au(acac)</td>
<td>dimethyl gold acetylacetonate; dimethyl (acetylacetonate) gold (III)</td>
</tr>
<tr>
<td>MFM</td>
<td>magnetic force microscopy</td>
</tr>
</tbody>
</table>
\( M_S \) saturation magnetization

\( n \) refractive index

\( \text{OL} \) overlap

\( \text{PBG} \) photonic band gap

\( \text{PLD} \) pulsed laser deposition

\( \text{PPMS} \) physical property measurement system

\( \text{RID} \) relative interaction diameter

\( \text{RMS} \) route-mean-square

\( \text{RT} \) room temperature

\( \text{SE} \) secondary electrons

\( \text{SEM} \) scanning electron microscopy

\( \text{SNS} \) suspended nanostructures

\( \text{SPM} \) scanning probe microscopy

\( \text{SQUID} \) superconducting quantum interference device

\( \text{STEM} \) scanning transmission electron microscopy

\( \text{STM} \) scanning tunneling microscopy

\( \text{Ta(OEt)_5} \) tantalum pentaethoxide

\( \text{TEM} \) transmission electron microscopy

\( \text{TEOS} \) tetraethyl orthosilicate; tetraethoxysilane

\( \text{TLD} \) thru-the-lens detector

\( \text{TMOS} \) tetramethoxysilane

\( \text{TMS} \) tetramethylsilane

\( \text{TTIP} \) titanium tetraisopropoxide

\( \text{UHR} \) ultra high resolution

\( V_a \) volume after annealing

\( V_b \) volume before annealing

\( V_l \) relative volume loss

\( \text{WDXS} \) wavelength-dispersive X-Ray spectroscopy

\( \rho \) resistivity

\( 2D \) two-dimensional

\( 3D \) three-dimensional
# CONTENTS

Abstract .......................................................................................................................... i  
Acknowledgements .......................................................................................................... iii  
Supplements ...................................................................................................................... v  
Nomenclature, abbreviations and denotations .................................................................. vii

## PART I: THESIS

Chapter 1: Introduction ................................................................................................. 1  
1.1. Motivation and Objectives ..................................................................................... 1  
1.2. Framework of the Thesis ....................................................................................... 2

Chapter 2: Literature Survey .......................................................................................... 5  
2.1. Introduction into EBID ............................................................................................ 5  
2.2. Advantages of EBID .............................................................................................. 6  
2.3. Versatility of Patterned Geometries ...................................................................... 8  
2.4. Some of Common Gas Chemistries Used for EBID ............................................... 11  
2.5. EBID Constraints .................................................................................................. 13  
2.6. Purification Strategies ........................................................................................... 16  
2.7. Application Areas of EBID-Grown Materials ....................................................... 17

Chapter 3: Experimental Setups and Characterization Techniques ....................... 23  
3.1. General Overview of Samples Preparation Approach ......................................... 23  
    3.1.1. Dual Beam Nova 600 NanoLab – the instrument for nanofabrication .......... 23  
    3.1.2. Deposition parameters .................................................................................. 26  
    3.1.3. Vacuum conditions for deposition process ................................................ 27  
3.2. Structural, Compositional and Topographical Characterization of EBID-Grown  
    Materials .................................................................................................................. 28  
    3.2.1. SEM analysis ................................................................................................. 28  
    3.2.2. FIB-SEM cross-sectional studies ............................................................... 28  
    3.2.3. Sample preparation for TEM investigation ................................................ 29  
    3.2.4. HRTEM characterization ............................................................................. 30  
    3.2.5. EDXS analysis .............................................................................................. 31  
    3.2.6. 3-dimensional topographical AFM studies ............................................... 31  
3.3. Analysis of Functional Properties ......................................................................... 32  
    3.3.1. Magnetic and magneto-transport studies .................................................... 32  
    3.3.2. Electrical measurements ............................................................................. 32  
    3.3.1. Optical properties’ characterization of insulating EBID patterns .............. 32  
3.4. Complementary Pre- and Post-Processing Techniques ........................................ 33  
    3.4.1. Buffer layers deposition via PLD method ................................................... 33  
    3.4.2. Heat treatment of as-deposited EBID structures ....................................... 34  
    3.4.3. Cleanup wet etching ..................................................................................... 35
Chapter 4: Results and Discussions ................................................................. 37

4.1. Aspects of EBIDs’ Purity Enhancement via Deposition at Elevated Temperatures
of W-, Si-, Pt-, Co-, and Au-based precursors ....................................................... 37

4.2. Nano- to Micro-Scale Patterning of Pure Cobalt ............................................ 44
   4.2.1. Combination of EBID and seeded growth at elevated temperatures from
          Co\textsubscript{2}(CO)\textsubscript{8} precursor ................................................................. 44
   4.2.2. Magnetic and transport properties of the Co EBID and seeded
          structures ........................................................................................................ 49

4.3. EBID of Gold from Me\textsubscript{2}Au(acac) Precursor. Purification and Shape Control .. 51
   4.3.1. Purification and shape control approaches for creation of planar
          nanoscale Au structures ................................................................................... 51
   4.3.2. Tailoring of deposition vs. annealing conditions to form high aspect ratio
          periodic Au nanopatterns ................................................................................. 57
   4.3.3. Cleanup wet etching step for further device application ......................... 60

4.4. Nanopatterning of Si-Based Insulating Materials via Gas-Assisted EBID ...... 63
   4.4.1. Oxygen-assisted EBID from TEOS precursor: challenges and
          discoveries ........................................................................................................ 63
   4.4.2. Studies of optical properties ..................................................................... 65
   4.4.3. Electrical measurements of the SiO\textsubscript{2+δ} EBID-grown material .......... 66

4.5. Nanofabrication of Ultra-Sharp AFM Tips via EBID from Naphthalene
    Precursor ............................................................................................................ 69

Chapter 5: Conclusions and Perspectives ............................................................ 73

5.1. Conclusions .................................................................................................... 73
5.2. Outlook to the Future ..................................................................................... 74
5.3. References ..................................................................................................... 75

PART II: SUPPLEMENTS
1.1. Motivation and Objectives

Our world is not static. Changes and developments are taking place every day. Thus during the previous century scientific and technological progress led to development of almost all the devices and goods that we are using in our daily life: from a mixer to an aircraft. One of the fields that expanded dramatically and enabled in-depth analysis and detailed visualization of structure and functional properties was microscopy! Among the most fascinating advancements is certainly going beyond imaging and 3D visualization to modification of the surface. One such modification is the ability to grow nanoscale structures of different materials inside the chamber of the microscope by means of Electron Beam Induced Deposition (EBID).

EBID itself is quite a versatile process, which allows scientists to experiment with a number of different gas chemistries, e.g. for creation of conducting, insulating and magnetic structures. In most of the cases precursors used for EBID process are of organometallic nature, and ideally after a local decomposition by the effect of an electron beam, non-volatile functional material should be adsorbed to a substrate’s surface and the rest should constitute a volatile part which should be pumped away by the vacuum system of a microscope. Unfortunately in practice as-deposited structures consist not only of the functional material intended for deposition, but also contain large amount of carbonaceous matrix, due to incomplete decomposition of the precursor molecule. This phenomenon significantly affects functional properties of the deposited materials and limits their application range. To reduce the amount of contamination in the grown samples, specific purification steps should be applied, depending on the selected precursor [1–4].

Considering the actual demands for functional nanomaterials in the fields of micro- and nano-electronics, plasmonics, photonics, spintronics, bio-technology, biosensing and life sciences, the main focus in our research work was made on the following gas chemistries:

- dimethyl gold acetylacetonate (Me₂Au(acac)) for Au deposition,
- dicobalt octacarbonyl (Co₂(CO)₈) for Co patterning,
- tetraethyl orthosilicate (Si(OC₂H₅)₄) (TEOS) for SiO₂ fabrication.
The primary objective of this project was to develop purification routines for EBID from these chemicals, optimize the processing parameters and study structural and functional properties of the deposited materials. Enhancement of chemical composition was a common goal for all three precursors, but besides it for each gas chemistry separate achievement targets were also set, in particular:

a) For Au-based EBIDs the focus was made on the minimization of undesirable structure reconfiguration, as a side effect of ex-situ post-annealing purification step.

b) For the Co-based EBIDs we were aiming to achieve as good magnetic and transport properties of nanopatterned structures, as close as possible to the bulk material.

c) For the SiO$_2$-based EBIDs the purpose was to create carbon-free amorphous insulating Si-oxide, with the absorption and refraction properties comparable to conventional silica glasses.

Besides, select purification studies for MeCpPtMe$_3$ and W(CO)$_6$ precursors were also conducted, but they did not lead to significant purity improvement of the deposited materials.

We evaluated some applications of the EBID nanopatterns. One example was nanofabrication of ultra-sharp carbon AFM tips via EBID from naphthalene precursor. Durability and resolution of the tips were studied.

1.2. Framework of the Thesis

The thesis can be nominally divided into 5 parts. Chapter 1 shortly describes motivation of the started work and lists its objectives. Chapter 2 gives a brief introduction into the EBID world, presenting advantages and constraints of this method, mentioning application areas and existing purification approaches of the deposited materials. In Chapter 3 the reader may find an overview of the experimental setups and characterization techniques, including information about the nanofabrication process and the tool itself, aspects of structural, compositional and topographical characterization of EBID-grown materials, as well as information about subsequent analysis of functional properties, and description of additional pre- and post-processing techniques. Chapter 4 is basically the main part of the thesis. It
presents results and discussion of the accomplished work and can be divided into 5 sub-chapters. Chapter 4.1 gives an overview of our systematic evaluation of the purification approach for the deposits from W-, Si-, Pt-, Co-, and Au-based precursors via EBID at elevated substrate temperatures. The further three sub-chapters 4.2, 4.3 and 4.4 summarize results of our research work aimed towards nanopatterning of pure cobalt, gold and silicon dioxide respectively. Chapter 4.5 describes our achievements in the field of ultra-sharp AFM tips’ nanofabrication via EBID from naphthalene precursor. General conclusions and further perspectives of our program, as well as bibliographic list can be found in the Chapter 5. The thesis ends with the attached supplements of our published articles and manuscripts, related to the topic of the dissertation.
CHAPTER 2: LITERATURE SURVEY

2.1. Introduction into EBID

*Electron-Beam-Induced Deposition* is a complex nanopatterning method, taking its routes approximately from the times when original development of electron microscopes began. In particular the first report of contamination-based films growth observed in an electron-optical system was published by Steward in the 1934 [5]. Since that time, for several decades continuously, discoveries in the EBID area were going quite slow; and only in the end of the 1980-s the interest to electron-beam-assisted patterning started growing exponentially. Most likely, it is related to release of field emission guns, thanks to which resolution of electron microscopes improved dramatically and thus enabled higher precision of e-beam-assisted nanoprototyping.

Sometimes, to build up an analogy, electron-beam-induced deposition is called e-beam-induced CVD-like process [6–7], capable to create 3D nanostructures and being significantly more localized and controlled than conventional CVD method. In general *EBID* is based on a local decomposition of a precursor gas by the effect of a focused electron beam. Thus, in order to perform this three-dimensional direct-write process one would need to use an electron microscope (an SEM, TEM or a Dual Beam), equipped with a gas injection system (GIS), through which local delivery of precursor gas molecules will be done [1–3]. An overview of a standard GIS is shown in Figure 2.1 (left) [8] and schematics of the EBID process is illustrated in Figure 2.1 (right) [9]. In this thesis the main focus will be on the aspects of electron-beam-induced deposition performed in the chamber of a Dual Beam microscope or an SEM.

So essentially, when GIS is inserted in the vicinity of a sample, being only a few microns away from the substrate’s surface, its pneumatic valve should be open and precursor vapor phase molecules are introduced into the microscope chamber via a GIS needle. Then focused electron beam starts local rastering, within the boundaries of an identified pattern, and precursor molecules are dissociating under its effect: non-volatile precursor components are adsorbed to sample’s surface, volatile fragments are pumped away and a solid deposit is formed.

The major role during EBID process is played by secondary electrons, which originate from e-beam interaction with the sample, and by a competition between
chemisorption and physisorption reactions, that are strongly dependent on the combination of chosen precursor, substrate and deposition temperature [1–3]. Thus selection of the patterning parameters is crucial and significantly affects both deposition rate and purity, e.g. increase of operational current will result in the enhancement of deposition rate (unless the deposition is already limited by precursor supply) and elevation of accelerating voltage will visa verse lead to the rate’s drop, in most of the cases.

![Figure 2.1. (Left) A gas injection system with high re-positioning accuracy. Precursor is located in a crucible and supplied to the sample through a valve and a 500 µm wide needle [8]; (Right) Schematic overview of the EBID process [9].](image)

### 2.2. Advantages of EBID

Development of EBID significantly widened manufacturing possibilities for modern scientists and opened doors to the new level of micro- and nano-fabrication.

First of all nowadays this process enables true **nanoscale** prototyping, with an ultimate **shape control** in x, y and z directions, going beyond simple 2D limits to an advanced tailoring of **3D** nanostructures with preferred orientation and functional properties [10].

As well EBID allows **precise positioning** of the desired deposits, enabling their **site-specific** patterning both on flat and **topographical surfaces**: e.g. scanning probe microscopy (SPM) tips manufacturing [10–11] (see Figure 2.2), deposition of complex 3D nanostructures that requires application of high stage tilts [12], etc.
Even though deposition rates vary to some extent for different precursors, in case of e.g. individual nanostructure deposition, EBID process is quite rapid, especially since it does not require masks or any other additional steps, for instance, EBID fabrication of an MFM tip takes only a few seconds [10–11].

![Figure 2.2. SEM images of EBID-fabricated Co-based SPM tips, with the view at a 52° tilt (Left) an ultra-sharp Co EBID tip for HR MFM [11]; (Right) Co EBID tip with spherical symmetry for FMRFM [10].](image1)

At the same time, as one more advantage, patterning of as large areas as $\approx 100 \, \mu m^2$ at a max could be performed in a single operation, growing for example contacting wires, or protective layers for the in-situ FIB-SEM 3D reconstruction.

Besides, EBID is an additive process, which can consist of multiple steps for sculpting of complex geometries, synergizing numerous patterns of various shapes and sizes. Additionally EBID can make use of different gas chemistries, both simultaneously and successively without breaking vacuum, thus resulting in a fabrication of multi-component systems, combining both conducting and insulating structures [13].

It overcomes fundamental resolution limits of conventional electron-beam lithography [14–15]. No sharp and uneven edges are observed as after lithographical resist etching or lift-off procedure, vice versa the sides of EBID-created patterns are quite sloping, as shown in Figure 2.3. As well, most of the conventional lithographical methods result in high roughness of the exposed substrate, while during EBID original nano- to pico-meter smoothness can be preserved.
One more advantage of the e-beam-assisted deposition is that taking into account the fact that nanoprototyping process itself is done inside the chamber of an electron microscope, direct structural observations and compositional studies of the patterned specimen can be performed straight inside the same instrument right after the deposition process is over.

**Figure 2.3.** SEM images of as-deposited SiO$_{(2\pm\delta)}$ pads after FIB cross-section analysis, with the view at a 52° tilt.

The last, but not least, benefit of electron-beam-induced deposition is that, in those cases when a microscope is equipped with a nanomanipulating system (e.g. Omniprobe) the local pick-up, seal, transportation and mounting of various objects from one location to the other can be easily performed in-situ in the chamber of a microscope via combination of EBID and FIB milling process. This approach is frequently used for the lamella preparation – a state-of-the-art Dual Beam manufactured sample for the TEM analysis (please see Chapter 3.2.3 for more details).

### 2.3. Versatility of Patterned Geometries

The geometry of EBID-grown patterns is truly versatile. It expands from creation of planar cuboids or lines up to three-dimensional nanowriting of complex species. Some examples of as-deposited structures are shown in Figures 2.2 – 2.7.
Most of the EBID structures are grown using either the SEM’s built-in **patterning engine**, if it exists, or an external one. In the patterning engine pattern sizes and shapes (e.g. line, circle, rectangle, polygon, etc.) can be identified, deposition rate or yield of the particular gas chemistry at a certain beam parameters (e.g. accelerating voltage and current) can be specified and such e-beam variables as dwell time (DT), overlap (OL), relative interaction diameter (RID), pitch, scanning direction and etc. can be adjusted depending on the desired final geometry of the deposit. This Thesis work was carried out using FEI built-in patterning engine.

**Figure 2.4.** AFM images (three-dimensional representation) of Au EBID patterns from Me₂Au(acac) precursor: example of *(Left)* cuboid and *(Right)* line deposition.

Advanced operational parameters such as dwell time, overlap and pitch are indeed rather important and give an operator quite many degrees of freedom, allowing the overstep **from basic built-in patterns up to non-standard shapes**. Thus, by increasing the values of **dwell time** and **overlap**, **complex 3D nanostructures** can be created, e.g. nanobridges (Figure 2.5, left), nanospirals, etc. Application of a specific **pitch** size can transform a simple cuboid structure (see Figure 2.4, left) into the array of dots or pillars (Figure 2.5, right).

EBID nanopatterning also allows prototyping of even more **non-trivial 3D structures** with highly controlled x, y and z dimensions, such as puzzles and gears (Figure 2.6), 3D logos (Figure 2.7) or even portraits, to name just a few (EBID-lithographed portrait of A. Botman can be found in ref. [9]). Such nanowriting is feasible thanks to application of **bitmap files**. Basically any bitmap picture can be
selected and imported in the microscope’s user interface. The main restriction is that the image should consist of only two colors, blue and black for example. The gradient of those colors will identify the thickness of the desired structure, and sophisticated 3D geometry will be clearly translated in a patterned deposit, within a single step operation.

**Figure 2.5.** Examples of complex 3D EBID-manufactured nanostructures

(Left) SEM image of a 3D Pt-EBID nanobridge (tilted view) [4, 9];
(Right) AFM image of as-deposited Au pillar array from the Me$_2$Au(acac) precursor at 5 kV, 1.6 nA (three-dimensional representation) [16].

**Figure 2.6.** SEM images of some 3D bitmap-patterned deposits from TEOS precursor, with the view at a 40° tilt: (a) a gear and (b) a puzzle.

For the EBID micromachining of larger area periodic nanostructures it is recommended to use scripted stream files, capable to perform ultra-high resolution
positioning of every single feature in the pattern through a complete control over the beam trajectory.

With the novel developments in the area of field emission gun systems (FEG-SEMs) that allow fine manipulation of the e-beam diameter, utilization of immersion modes and ultra-high resolution focusing, the ultimate resolution levels of EBID structures can be achieved going down to pattern sizes of several nanometers. Thus, to obtain the finest EBID-written structures the e-beam diameter should be minimized [17]. To fulfill these requirements, operational accelerating voltage should be maximized and selected current should be as low as possible. For instance, as reported in reference [11], deposition of HR MFM tips from dicobalt octacarbonyl precursor at 30 kV and 150 pA in a spot mode resulted in a formation of ultra-sharp probes with the tip’s end diameter on the order of 20 nm (Figure 2.2, left). Even though the size of 20 nm is already impressive, it is not yet the final restriction for the EBID technique. This nanomachining process is capable to push its resolution limits down to deposits of 3 nm dots and even smaller, while creating Pt-based dot arrays (DA) as reported in [18].

![AFM image of a 10 nm thick Pt-EBID-bitmapped Asylum Research logo (three-dimensional representation).](image)

**Figure 2.7.** AFM image of a 10 nm thick Pt-EBID-bitmapped Asylum Research logo (three-dimensional representation).

### 2.4. Some of Common Gas Chemistries Used for EBID

In many of the cases precursors used for the electron-beam-induced deposition are the same that are usually utilized for the CVD process. Considering that majority of precursors are of the organometallic nature, structure of as-deposited material
typically consists of metallic nanocrystals embedded in the carbonaceous matrix, as shown in Figure 2.8, left. Commonly selection of the precursor is strongly dependent on the requirements to chemical composition of the final structure and the application area of the created sample. Most of the precursors are sensitive to air and moisture, thus loading of chemicals in a GIS crucible should be generally performed inside a glove box. As well special attention should be paid to the storage conditions of precursors (e.g. atmosphere, temperature, etc.), since some of them can decompose slightly above room temperature or oxidize after exposure to air, for instance. For the certain precursors the level of toxicity should be also taken into account, for safety reasons.

![Figure 2.8. (Left) TEM image of as-deposited Au EBID pad from Me$_2$Au(acac) precursor on a buffer layer, showing the fine structure of gold nanoparticles (lattice fringes are clearly visible) embedded in the carbonaceous matrix (light areas) [16]; (Right) graphical representation of the Me$_2$Au(acac) chemical formula.](image)

Basically all precursors utilized for EBID nanoprototyping can be classified according to the type of ligands that surround central atom of the precursor’s molecule [3], in particular: H, F, Cl, Br, I, CO and PF$_3$ ligands. The general classification of gas chemistries used EBID is shown in Table 2.1; examples of precursors for each class are also listed. Most of those precursors are used for deposition of metal- / carbon-based conducting or magnetic structures, but some of
Si-, Ti- and Ta-based chemicals, such as e.g. TEOS, TMOS, SiH₄, Si₂H₆, Si(CH₃)₄ (TMS), TiCl₄, TTIP, Ta(OEt)₅, and etc. are utilized for the e-beam induced patterning of insulating materials.

One more categorization of precursors can be done as well taking into consideration their physical state, such as: powder (for ex. Me₂Au(acac)), gel (for ex. MeCpPtMe₂) and liquid state (for ex. TEOS). In some case carbon-free precursors are also classified as a separate group [4].

**Table 2.1. Classification of precursors for EBID according to ligands’ type.**

<table>
<thead>
<tr>
<th>Precursor’s type</th>
<th>Ligands’ type</th>
<th>Examples of precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrides</strong></td>
<td>H</td>
<td>C₁₀H₈, SiH₄, Si₂H₆, Ge₂H₆, GaN, D₂GaN₃</td>
</tr>
<tr>
<td><strong>Halides</strong></td>
<td>F, Cl, Br, I</td>
<td>WCl₆, WF₆, SnCl₄, TiCl₄, AuCl₃, SiCl₂H₂</td>
</tr>
<tr>
<td><strong>Carbonyls</strong></td>
<td>CO</td>
<td>Co₂(CO)₈, Fe(CO)₅, Fe₃(CO)₁₂, Ni(CO)₄, W(CO)₆, Cr(CO)₆, Mo(CO)₆</td>
</tr>
<tr>
<td><strong>Phosphines and Halogenophosphines</strong></td>
<td>PF₃</td>
<td>Pt(PF₃)₄, Ni(PF₃)₄</td>
</tr>
<tr>
<td><strong>Phosphines and Halogenophosphines</strong></td>
<td>Cl and PF₃</td>
<td>AuClPF₃, RhCl(PF₃)₂, Rh₂Cl₂(PF₃)₄, Ir₂Cl₂(PF₃)₄</td>
</tr>
<tr>
<td><strong>Organometallics</strong></td>
<td></td>
<td>Metal alkyls: Si(CH₃)₄ (TMS), Al(CH₃)₃, Sn(CH₃)₄. Sandwich aromatic or pseudo-aromatic complexes: Cr(C₆H₆)₂</td>
</tr>
<tr>
<td><strong>Acetylacetonates</strong></td>
<td>O₂ – Me bond</td>
<td>Me₂Au(acac) (Figure 2.8, right)</td>
</tr>
<tr>
<td><strong>Alkoxides, Nitrates, and Amides</strong></td>
<td>Organic ligands</td>
<td>TEOS, TMOS, TTIP, Ta(OEt)₅</td>
</tr>
</tbody>
</table>

2.5. EBID Constraints

Even though EBID process has quite many benefits, it still has some percentage of constraining factors as well. First of all, comparatively to other lithographic techniques, this process is limited by time and area of exposure, which in turn significantly affects the aspects of mass production process. In particular, due to the low EBID growth rates of some chemicals, patterning of areas larger than 100 µm² in
a single operation is rather time-consuming and is recommended to be split in several sequential steps.

Additional inconvenience is coming from the fact that, as in all areas of gas chemistry application, *precursors for deposition should be handled with special care and attention* to avoid their premature decomposition or degradation; in particular utilization of a glove box is necessary for majority of them. Some of the precursors have rather high level of toxicity and thus should be treated with extreme caution, e.g. halide-based chemicals, which are also corrosive and therefore not top-most preferred precursors for EBID, even though they generally result in reasonably high concentration of metallic constituent.

Another drawback of e-beam induced deposition process is that it frequently leads to formation of a so-called halo or an undesirable *overspray* around patterned area due to the effect of backscattered electrons (BSE) and chemisorption reactions which activate with the local overheating of the surface for deposition. Thus, halo size strongly depends on the selected precursor, substrate, deposition temperature, duration of prototyping and other deposition parameters, such as accelerating voltage and current (see Figure 2.9).

![Figure 2.9. SEM images of EBIDs examples: (Left) a pad grown from TEOS precursor at room temperature; (Right) lines grown from Co$_2$(CO)$_8$ precursor at 40 °C substrate temperature. The overspray around deposits is marked with arrows.](image)

As for the majority of cutting edge nanotechnology applications, the setup used for EBID is rather *complex* and does not allow full automation of the fabrication
process, thus, strongly requiring high user qualification. This additional restricting factor makes EBID process being extra time-consuming and almost impossible to perform without human participation.

To begin with, most of the precursors have individual sublimation and evaporation rates, when they are located inside a closed crucible of a GIS. Thus, they require special arrangements while opening valve first time, i.e. prior to an automated opening of a GIS pneumatic valve through software’s user interface, its manual outgassing by an operator should be performed. Thereby opening value of a pneumatic valve can be regulated and pressure level of introduced gas molecules inside a microscope chamber can be continuously monitored and adjusted. Otherwise microscope’s vacuum system might be strongly affected, and more over degradation of the electron beam filament can occur. For example, precursor for Co patterning dicobalt octacarbonyl − Co$_2$(CO)$_8$ has large amount of hexane (used to stabilize this compound for transportation and storage), which has high evaporation rate and thus leads to significant initial pressure jump; thus, this gas chemistry should be manually outgassed for several minutes prior to the deposition process.

Quite often nanopatterning is taking only a few seconds and should be performed in multiple areas on top of originally three-dimensional substrate, with additional application of stage tilts to enable creation of complex 3D nanostructures. In such cases automated nanoprototyping cannot be accomplished unfortunately and continuous participation of highly qualified operator is required, who must perform manual alignment and focusing procedure, as well as adjustment of patterning parameters at every step; otherwise precision of desired nanoscale dimensions of EBID-grown materials might be lost and more over GIS needle might be damaged due to local working distance change related to unevenness of substrate’s top surface. Same precautions, including local positioning with the e-beam shifts during real-time observation process, should be taken while performing depositions on top of semiconducting or insulating specimens, during which undesirable drifts can occur due to charge accumulation, leading to distortions in the fabricated geometry. However, in certain cases of nanomachining on top of ideally flat, uniform and well-grounded specimens, scripting files could be used, when local overpressure of gas chemistry is not an issue.
The last but not least EBID constraint is related to problems with the purity of as-deposited materials. In particular, even though in theory it is assumed that only non-volatile components of precursor should stick to surface after dissociation process, usually a deposit contains large amount of volatile by-products, which originally exist in the precursor’s gas molecule (e.g. C, O, H, etc. depending on the type of gas chemistry). This phenomenon leads to low concentration of the metallic constituent and high amount of impurities in a deposit, which strongly affect functional properties and therefore application areas of the EBID fabricated materials. Over the past decades different purification approaches of e-beam induced structures have been developed and their brief description will be presented in the next sub-chapter.

2.6. Purification Strategies

Purity of EBID grown samples is indeed very crucial aspect. It plays the main role in shaping of the destiny of patterned structures, i.e. selection of further application areas based on their functional properties. In general, chemical composition of the deposited materials strongly depends on the chosen precursor, substrate, many deposition parameters (accelerating voltage, beam current, deposition time, dwell time), vacuum conditions and possible post-treatment procedures applied to the deposited structures [1, 4]. Considering what precursor is used for the nanofabrication process, various purity enhancement strategies can be applied to the e-beam induced deposits, in particular [16]:

- annealing of as-deposited structures ex-situ [16, 19, 20] or in-situ [4] in the chamber of a microscope used for patterning,
- EBID onto a pre-heated substrate [8, 21–23],
- gas- [3, 23–27] or water-assisted [8, 12, 19, 28–30] electron-beam-assisted deposition,
- EBID in ultra-high vacuum (UHV) set-ups [31, 32]
- deposition from carbon-free precursor or aqueous solutions [33],
• alteration of deposition parameters [34] as well as variation of precursor’s pressure and temperature [4],

• in-situ or ex-situ post-treatment of deposited structures (for instance, annealing in the presence of second gas [9, 35, 36], treatment with atomic hydrogen [37], post-irradiating the deposit with electron beam [28, 38], Ga\(^+\) ions implantation [39], low temperature ozone or ozone/water treatment [40], O\(_2\) plasma treatment [41]).

One more way to enhance purity of as-deposited samples is basically to use an alternative source of charged particles, or simply to replace electrons with ions. Such process is called Ion-Beam-Induced Deposition, or shortly IBID, and it can be treated as EBID’s twin brother [3]. Basically, IBID can be performed in a focused ion beam (FIB) or a Dual Beam microscope, liquid metal ion source (LMIS) of which is mostly often based on Ga\(^+\) ions. On average this process results in a larger amount of metallic consistent than EBID, due to the high mass of ions, that induces faster dissociation of precursor molecules and local substrate heating. But on the other side this direct-write patterning also leads to an undesirable implantation of Ga\(^+\) ions, which as well affects the properties of grown structures, especially in the case of insulators nanoprototyping [42–44]. Moreover, during IBID following side effects should be also accounted, such as, possible top surface damage, worse resolution capabilities than with EBID and competition between milling and deposition, since FIB is originally designed for materials removal via local milling and sputtering and thus density of current should be considered for IBID process [45].

2.7. Application Areas of EBID-Grown Materials

Evidently, the electron-beam-induced deposition is a very unique and truly versatile state-of-the-art field, which discovery can be marked as a breakthrough in the modern world of rapidly growing nanotechnological areas. Thus, thanks to EBID, nowadays, ever tiny conducting, insulating and magnetic 3D nanostructures can be rapidly patterned on a wide variety of substrates with ultra-high precision, in a single operation, and without application of any masks. Even despite the fact that this
nanoprototyping technique still has some drawbacks (e.g. purity and growth rate issues, etc.), its direct-written structures has already found their potential and practical applications in a number of areas ranging from nanoelectronics to microbiology.

Probably the most simple and primary usage of EBID structures in a Dual Beam microscope is:

➢ **Deposition of protective layers** for cross-sectional studies, lamella preparation and FIB-SEM 3D reconstruction, frequently utilized for in-depth structural investigation (more details regarding these processes will be discussed in Chapters 3.2.2 and 3.2.3). Basically majority of EBID application areas can be classified as follows [3]:

➢ **Photo-masks’ repair** [46–49].

Considering the costliness of photolithographic mask sets, repair of damaged masks is more recommended than their re-writing. Therefore, electron-beam-induced deposition of opaque and transparent materials is a quite promising method to be applied for this purpose, particularly due to its capability to perform local site-specific patterning.

➢ **Fabrication of scanning probe microscopy (SPM) tips** [10, 11, 50–60].

Size, shape and aspect ratio are one of the most important quality parameters of SPM tips. In majority of the cases these factors directly influence resolution of acquired images. Thus, thanks to EBID’s ability to create ever small structures in a precise location, fabrication of SPM tips occupies fairly stable niche in the application range of E-beam-assisted prototyping. As in topographical studies (e. g. AFM, STM), so in the functional imaging (e. g. MFM, FMRFM, etc.), EBID-fabricated tips had already proven their leading positions. For example, C EBID can be used for manufacturing of high-aspect ratio durable tips, as will be discussed in Chapter 4.5; standard Co EBID, in its turn, makes superb MFM tips (Figure 2.2, left) [11], performance of which is significantly superior to the best commercial MFM tips available on the market (Figure 2.10).

Moreover, nowadays Co EBID can be also applied to deposit tips for ferromagnetic resonance force microscopy (FMRFM) – a novel unconventional nanoscale characterization approach, combining ferromagnetic resonance analysis with atomic force microscopy. Utilization of Co EBID tips in this method noticeably pushes conventional resolution and functionality limits, due to weaker stray fields of
rather small tips (down to below 100 nm in diameter, see Figure 2.2, right), therefore, opening the doors to new level of imaging techniques of magnetic nanostructures [10].

![MFM images of the same area of a Co-Cr “blank” magnetic recording film](image)

**Figure 2.10.** MFM images of the same area of a Co-Cr “blank” magnetic recording film: *(Left)* made by the best available commercial MFM tip (from Asylum Research Company, USA), *(Right)* made with a Co EBID tip (Images courtesy of Prof. Belova L. M. [11]).

➢ **Editing of integrated circuits** [61].

In circuit editing, application of FIB and EBID techniques is indispensable. In particular, EBID can be utilized for high-precision local deposition of both metallic and insulating pads and pillars to repair damaged areas of a circuit. In this process one of the common important requirements should be complied: deposited conductors necessarily should form a Schottky barrier with an underlying semiconducting substrate, for example GaAs. For that purpose EBID is strongly dominating IBID due to the fact that residually implanted ions into the fabricated structure result in an Ohmic behavior of a junction [62].

➢ **Nanophotonics** [19, 20, 29, 40, 44, 63–69].

The main requirements to the materials utilized in the nanophotonics area are low damping losses for the high metal purity plasmonic structures and combination of low absorption together with high refractive index for insulating photonic band gap (PBG) structures. The latest developments in the EBID area led to significant improvement of functional properties of fabricated materials, and therefore allowed their application for the nanophotonic industry. Thus, during the past years there had been
several reports in literature regarding electron-beam-induced nanoprototyping of plasmonic resonant structures [19, 29, 40, 63–65]. Attempts to deposit transparent nanooptic patterns [20] and high refractive index materials, such as silicon dioxide, for instance [66] have been also presented, as well as fabrication of the probes for near-field optical microscopy [44, 67–69] and photonic crystals [69]. Evidently, all those contributions clearly show that there is a high demand for utilization of EBID grown materials in the nanophotonics area.

**Micro- and nano-electronics** [3, 13, 22, 24, 70–79].

Basically, the application range of EBID materials in the micro- and nano-electronics is rather wide and it extends from insulators [24] and resistors to conductors. For insulating materials the main requirement is possession of high resistance, high breakdown voltage fields, and low intrinsic charges; while for conductors it is vice versa, low resistance with or without Schottky barrier contact, depending on a specific application [3].

Starting from the end of past century, e-beam patterned structures are gradually finding more and more applications in the following areas of micro- and nano-electronics as: nanoprototyping of hall sensors [22, 70], deposition of electrical contacts [71, 72] and conducting nanowires [73–76], including direct wiring of carbon nanotubes (CNTs) [71], patterning of electrical contacts to which is usually rather difficult, because frequently individual CNTs are randomly dispersed and oriented. As well thanks to the unique possibility of EBID to combine deposition of different gas chemistries in-situ in the same microscope chamber without breaking vacuum, diode-like structures [13, 77], and miniature tunnel junction devices [78, 79] can be also created using this versatile approach.

**Mechanical applications** [80–90].

In principle, mechanical applications of the electron-beam-induced patterning can be related to the soldering and nanomanipulating steps that require high deposition precision and accurate navigation, as in the case of TEM lamella preparation or handling of carbon nanotubes, for instance. Thus, EBID had already been implemented for contacting CNTs and nanowires with conducting and non-conducting materials [80–82]; it was used for their placement onto AFM tips or micro-electromechanical system (MEMS) structures [83–88], e.g. to serve as the emitter source for deposition process [86], or to contribute to the mechanical testing
of nanotubes and nanowires [84−85]. Also electron-beam-assisted nanoprototyping was utilized for creation of seeded layers for CNTs growth [89]; as well as for the fabrication of nanotweezers devices [90].

➢ *Field emitters* [21, 91−106].

Quality of an electrons source is directly affecting the level of imaging resolution in any SEM and TEM. Thus, for the couple of past decades, aiming towards the highest resolution index, leading positions in this area were occupied by field emission guns or shortly FEGs, among all other sources used for electron microscopy. One of the main requirements to the FEGs is the ultimate sharpness of the tip, from which electrons are emitted. Considering that EBID is capable to create high-aspect ratio sharp tips of various materials, its application for fabrication of field emitters laboratory prototypes has been tested already in the 1990-s. After a numerous trials it turned out that EBID tips, fabricated out of Au-, C-, Mo-, Pt- and W-based precursors, result in high emission currents at low voltage, good beam confinement and high field enhancement.

➢ *Mask fabrication for pattern transfer* [16, 61, 107−112].

The need of masks fabrication is indispensable for the majority of lithographical applications. In most of the cases materials used for this purpose should be stable against dry or wet etching. As it was demonstrated in [16, 61, 107−112] EBID grown structures fulfill following requirement and has a high potential to be utilized in this area. Moreover, EBID’s high-precision selectivity during deposition process should be noted as well, thanks to which advanced 3D patterns can be also fabricated.

➢ *Bio-related applications* [9, 29, 113].

Application of EBID manufactured nanostructures in the fields of medicine and biotechnology is rather hot, but relatively new topic. In particular the high interest in this area is attracted to EBID nanopatterning due to its possibility to grow planar and 3D nanostructures of the preferred orientation and location. The range of used precursors for this purpose is rather wide and thus insulating or conducting materials can be deposited. Further attachment of functional groups to them, such as silanes to silicon dioxides and thiol groups to gold structures, for instance, would serve as an additional anchoring layer to activate affinity of this materials to bio-molecules, e. g. protein filaments or DNAs to name a few. Such type of immobilization approach in life science would result in a dramatic improvement of biological tissue imaging and
properties characterization. However, even though this application area of EBID seems to be quite promising, until now there were only a few reports in literature discussing aspects of biocompatible tests for EBID grown structures. Most likely it indicates that this application field is quite nontrivial and that extensive research in it is still ongoing.

So, to summarize, it is quite obvious that all listed above applications of fascinating EBID technique once again prove its uniqueness and main advantage of this direct-write site-specific 3D nanopatterning. In principle this technique provides practically unlimited degrees of freedom to perform well-controlled local nanostructuring of functional materials, designing the desired nanoconfiguration with tailored properties. Moreover, as compared to other synthesis or deposition approaches used for nanoprototyping, EBID allows creation of nanostructures not only in groups, but also individually (e.g. nanodots, nanopillars, etc.), and at a designed location, introducing capability of a single nanostructure’s full characterization. Earlier it was not really possible for majority of other nanofabrication methods, therefore demonstrating clear evidence of EBID’s advantage and its contribution to remarkable widening of nanotechnology horizons.

It certainly appears that EBID is the future of advanced functional nanoprototyping! However, its problems with chemical composition of deposited structures are still quite a limiting factor; obviously highlighting that further development of purification strategies of EBID patterned materials is strongly desired. Thus, further improvement of their chemical composition, will most likely enhance their functional properties and therefore, transform their potential applications into the real industrial manufacturing. This is especially true since already at this stage, being at times heavily contaminated with the dissociation by-products, EBID grown materials were suitable enough for a majority of applications listed above.
CHAPTER 3: EXPERIMENTAL SETUPS AND CHARACTERIZATION TECHNIQUES

3.1. General Overview of Samples Preparation Approach

3.1.1. Dual Beam Nova 600 NanoLab – the instrument for nanofabrication

The age, where science fiction becomes reality, has come!

Continuously growing scientific interest to learn more about the structure and properties of the surrounding us materials and life organisms, perform their 3D in-depth studies and to create own nanoscale structures with tailored properties led to unbelievable discoveries in the area of high-resolution microscopy. Starting from the first LOM’s prototype – the Galilean’s telescope developed in the 17-th century – until today a whole constellation of novel imaging techniques was born, such as: TEM, SEM, STEM, FIB, SPM, to name just a few.

Existing separately from the middle of the 1970-s, high-resolution FEG-SEM and Ga-based FIB were capable to provide researchers with useful information about fine structure of investigated samples, however at the same time boundaries of their characterization were somewhat restricted. Thus, SEM was limited by the planar 2D topographical imaging, while FIB was able to open up the inner parts of specimens via local milling or materials sputtering with heavy Ga$^+$ ions, but on the other side it was suffering from undesirable ion beam damage during image acquisition, destruction of thin structure layers (i.e. sputtered films, corroded oxide layers, etc.), contrast / brightness adjustments and high-resolution focusing problems, as compared to SEM. In the beginning of the 21-st century these two cutting-edge technologies, SEM and FIB, were combined together in a single tool, called Dual Beam (or currently a more general name “combined FIB / SEM instrument”). Emerging of this know-how led to a total breakthrough in the area of 3D structure analysis and nanoprototyping, and feasibly met demands of modern research society to a large extent.

Essentially, since that time local FIB milling of materials with ions and sequential HR SEM imaging with electrons was merged in one instrument. That is how controlled 3D in-depth characterization was enabled, beginning from ordinary cross-
sectional studies and moving towards non-trivial lamella preparation for HR TEM analysis and HR 3D reconstruction of large volumes.

Like SEMs, majority of Dual Beam microscopes are also equipped with standard analytical devices, such as EDXS or WDXS for chemical composition analysis, EBSD for crystallographic studies, and etc. Thanks to them, in-situ 2D and 3D analytical investigations of different samples can be performed.

Figure 3.1. (Left) A photo of the Dual Beam Nova 600 NanoLab: FEB, FIB, GIS, nanomanipulator, EDX dewar, EBSD, cryo chamber and microscope chamber are denoted; (Right) Side view with schematic GIS ports location around FIB column (Image courtesy of FEI).

As well, in many of the cases, systems for supply of a local flow of selected precursor molecules to the sample’s surface are connected to combined FIB-SEM microscopes. These so-called GIS lines are usually applied for the site-specific 3D nanopatterning of metallic, semiconducting and insulating materials via electron- and / or ion-beam-induced deposition (EBID / IBID), where electrons or ions are utilized to dissociate precursor gas molecules respectively. Dual Beam microscopes can be also equipped with the cooling and heating stages. So, high-profile imaging and
nanoprototyping can be done not only in the controlled gas environment, but also at the variable temperatures, mostly ranging from liquid nitrogen up to \( \approx 300 \, ^\circ C \).

Evidently, all the above mentioned comprehensive capabilities of Dual Beam microscopes significantly broaden their application range (as compared to single beam FIB and SEM systems) covering such capabilities, as top-down machining and deposition, nanoscale prototyping, 2D and 3D characterization, analysis of nanostructures below 100 nm size, etc. This certainly supports the statement that a Dual Beam system is “a full nanotechnology lab within one microscope”, inside which materials can be created, modified and analyzed.

Particularly in our research we were using the Dual Beam system Nova 600 NanoLab from FEI (The Netherlands), outer and inner view of which is shown in Figures 3.1 and 3.2 respectively.

**Figure 3.2.** An inner view of the Dual Beam Nova 600 NanoLab chamber
(Image courtesy of FEI).
3.1.2. Deposition parameters

Considering that the main focus of the thesis work was on purification and shape control of the EBID-grown materials, a variety of deposition parameters and geometries were tested for the following gas chemistries:

- dimethyl gold acetylacetonate (Me$_2$Au(acac)) for Au deposition,
- dicobalt octacarbonyl (Co$_2$(CO)$_8$) and cobalt tricarbonyl nitrosyl (Co(CO)$_3$NO) for Co patterning,
- tetraethyl orthosilicate (Si(OC$_2$H$_5$)$_4$) (TEOS) for SiO$_2$ fabrication,
- naphthalene (C$_{10}$H$_8$) for C nanoprototyping,
- methyl cyclopentadienyl platinum trimethyl (MeCpPtMe$_3$) for Pt growth,
- tungsten hexacarbonyl (W(CO)$_6$) for W deposition.

Generally, to facilitate the most optimal purification dynamics and desired final structure formation of nanoprototyped materials, variation of such deposition parameters as accelerating voltage, current, deposition time, overlap, dwell time, geometry and size of patterns was done to a certain extent.

Thus, for instance, during the analysis of Au-, Co-, SiO$_2$-, Pt- and W-EBID onto a preheated substrate (described later in Chapter 4.1), mostly cuboids were created, of 1 × 1 and 2 × 2 µm$^2$, at 5 kV, 1.6 nA and 2 kV, 0.7 nA with 15 µs dwell time and 60% overlap, varying deposition time from 5 to 20 min, depending on the yield of the tested gas chemistries, to achieve the thickness of patterns appropriate for EDXS analysis.

For the seeded growth of Co pads and wires (see Chapter 4.2) accelerating voltages of 2 and 5 kV were selected with nominal current values of 0.84, 3.4 and 1.6, 6.3 respectively.

EBID from Me$_2$Au(acac) precursor (Chapter 4.3) was performed at 5 kV, 1.6 nA and 6.3 nA; 2 kV, 0.84 nA and 3.4 nA, 18 kV, 0.15 nA (UHR mode) and 20 kV, 0.15 nA. A variety of different shapes was patterned, such as: planar cuboids (or shortly pads), dot arrays (DA), pillar arrays and lines.

During nanofabrication of SiO$_2$ material, besides cuboids and pillars, advanced 3D structures were also patterned (Figure 2.6). The deposition parameters were ranged between 2 – 20 kV and 0.21 – 9.5 nA (Chapter 4.4).

For the creation of carbon EBID AFM tips accelerating voltage was varied from 5 to 30 kV utilizing as low current values as possible, to maintain the required 3D
geometry. After a series of tests the best nanopatterning results were found for the deposition at 18 kV, 0.6 nA in UHR mode (Chapter 4.5).

3.1.3. Vacuum conditions for deposition process

From literature it is known that variations of the vacuum conditions play a significant role in purity control of the electron beam deposits [3, 4, 8, 9, 31, 32]. To give one example, here is how, based on our experience, composition of Co EBID patterns depends on the vacuum conditions (with strongest effects in this case being residual hydrocarbons and residual water vapor) (see Table 3.1).

\textbf{Table 3.1.} Effect of vacuum conditions on composition of Co EBID patterns.

<table>
<thead>
<tr>
<th>Substrates in the chamber overnight</th>
<th>Substrates in the chamber after plasma-cleaning the chamber for 2 h</th>
<th>Substrates in the chamber after plasma-cleaning the chamber for 2 h and kept overnight</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deposition parameters</strong></td>
<td><strong>C (at.%)</strong></td>
<td><strong>O (at.%)</strong></td>
</tr>
<tr>
<td>5 kV 1.6 nA</td>
<td>22</td>
<td>20.5</td>
</tr>
<tr>
<td>5 kV 6.3 nA</td>
<td>20.9</td>
<td>18.2</td>
</tr>
</tbody>
</table>

Thus, for the best data reproducibility, the following preparatory samples’ handling routing was chosen:

1) Where possible eliminate utilization of standard carbon or silver paint, carbon tabs or any other sticking material, to avoid additional out-gassing of any kind. Instead clamp the substrate to a holder with clips.

2) Subject the sample to an overnight pumping via mounting it inside a microscope’s chamber the evening before the experiment the next day.

3) After overnight pumping vacuum pressure level in the chamber should be $\cong 2 - 3 \times 10^{-6}$ mbar or less.

4) If a microscope is equipped with the cryo-can cold trap (as in our case), fill it with LN$_2$ and wait for at least 15 min, to minimize the level of residual water vapor in the chamber. Ideally pressure should go down to $\cong 1.1 \times 10^{-6}$ mbar.
5) If a sample is mounted on top of a heating stage, do substrate preheat to 130 ºC for several minutes with subsequent cool down to RT, to remove residual water adsorbed on a substrate’s surface.

3.2. Structural, Compositional and Topographical Characterization of EBID-Grown Materials

3.2.1. SEM analysis

Primary structural characterization of fabricated patterns was done via SEM and HR SEM analysis utilizing a same Dual Beam system.

Aiming towards the highest resolution, majority of SE images was acquired in UHR mode preferably using 18 kV, 0.15 nA.

To get the best understanding of patterned geometries, planar top view SEM analysis was combined with tilted view imaging that provided basic information about 3D topographical features, such as e.g. high-aspect ratio pillars and pads.

Some examples of HR SEM images were previously shown in Figures 2.2, 2.3, 2.6 and will be later presented in the Thesis as well (e.g. Figures 4.24, 4.33, 4.34).

3.2.2. FIB-SEM cross-sectional studies

In order to perform HR in-depth studies of patterned structures, including characterization of their homogeneity, deposit-to-substrate interface and profile judgment of deposit’s geometry, site-specific FIB-SEM cross-sectional analysis was utilized.

Basically this process consisted of 3 steps:

1) In-situ localized EBID of Pt layer on top of a feature of interest to protect it from harmful FIB ions’ effect and to even out the top surface of a deposit, thus, avoiding undesirable curtaining phenomenon, comprising in traces formation from each significantly sticking out feature during subsequent milling step.

2) FIB milling or sputtering to open up the volume laying in front of the patterned sample for analysis.

3) SEM imaging of created cross-sectional view, revealing in-depth information about structural features in the third dimension (e.g. Figure 2.3).
3.2.3. Sample preparation for TEM investigation

For the TEM analysis 2 types of samples were used:

1) SEM-FIB machined lamellae mounted at the bar of a dedicated Cu grid, each being a cross-section of the patterned deposition.

2) Thin pillars grown directly on the top surface of a Cu grid, pre-polished with the FIB.

Itself, among all existing nowadays TEM sample preparation routines, lamella fabrication via FIB is a quite unique approach due to its site-specificity, and apparently it is the only method used for manufacturing of TEM specimens from e.g. MEMS and nanoprototyped devices. Moreover, lamella preparation process is significantly faster (at least by a factor of 2) than conventional TEM sample preparation routines, used for steel characterization, such as e.g. electrolytic thinning.

So in principle, this procedure can be conditionally divided into the following steps, in the beginning being somewhat similar to the cross-section preparation, described in Chapter 3.2:

1) Pt EBID protective layer deposition followed by Pt IBID, which has higher deposition rate than EBID and thus results in faster growth of reasonably thick protective layer, required for preparation of extensively exposed to ion beam lamella.

2) Material removal on both sides of the investigated sample via FIB milling, as shown in Figure 3.3(a).

3) Pre-thinned lamella undercut, sealed to nanomanipulator’s tip via Pt IBID and lift-off from substrate’s matrix (Figure 3.3(b)).

4) In-situ manipulator’s navigation and Pt IBID-assisted mounting of the pre-thinned lamella on top of the dedicated Cu TEM grid, located in the same microscope chamber (Figure 3.3(c)).

5) Final FIB-induced lamella thinning and polishing down to the required thickness (often below 30 nm) (Figure 3.3 (d)).

In the case of the second approach the main goal was to grow thin enough pillars, able to transmit electrons through them and long enough that the grid doesn’t interfere with the analysis. Following preparation method did not involve any additional fabrication steps, as in the case of lamella preparation, and, thus, was allowing eliminating potential undesirable amorphization artifacts that could appear during FIB milling and thinning procedures. In particular, pillars grown from TEOS and Me$_2$Au(acac) were characterized with TEM.
**Figure 3.3.** Schematic overview of SiO$_2$ EBID lamella preparation: (a) SEM image illustrating the initial site-specific definition of the lamella after FIB cuts were done on its both sides, with the view at a 55° tilt; (b) FIB image representing a nanomanipulator’s tip ending with a pre-thinned lamella, sealed to it with Pt IBID; (c) FIB image of a Cu TEM grid with mounted lamella; Pt GIS and nanomanipulator are denoted; (d) HAADF STEM image of final lamella, where protective layers, TEM grid, Si substrate and SiO$_2$ EBID sample are marked with arrows.

### 3.2.4. **HRTEM characterization**

TEM analysis of described samples was done using JEM-2100F (JEOL, Japan) and Technai G2 F20XT (FEI, The Netherlands) transmission electron microscopes.

Mostly TEM characterization combined TEM, STEM and HR TEM imaging, diffraction and FFT analysis, along with EDXS and in some cases EELS and energy-filtering studies.
3.2.5. EDXS analysis

To be able to measure the composition of the resulting deposition by EDXS, it is necessary to be able to discriminate between the elements in the substrate and the elements in the deposition. To this end, the deposition must be thick enough to avoid penetration of the primary beam at 5 kV analytical beam energy, while at the same time the x-ray lines of the elements in the deposition and in the substrate do not overlap. Even in this condition however, a base element in the substrate should not be present to more than 20% of the total net peak intensities, else by peak deletion the EDX-ZAF correction mechanism for transferring k-ratios into atomic percentage (correction for excitation, absorption and fluorescence), is no longer accurate.

In most of the cases deposition was done on top of Si substrates, however for chemical composition analysis of Si-based materials, Cu films were utilized instead to insure proper EDXS analysis. Because of rather small dimensions of produced patterns, their elemental composition was determined by EDXS analysis both in SEM and TEM.

In the dual beam system the EDXS measurements were performed at 5 kV, 0.4 nA using an Oxford Inca EDXS system. To ensure a proper excitation volume, thus avoiding the signal from the substrate, the thickness of the structures was matched with the Monte Carlo simulated penetration depth of the electron beam in the structure. In the TEM analysis was done at 200 kV, 0.2 nA in STEM mode using an EDAX EDXS system.

3.2.6. 3-dimensional topographical AFM studies

Volume calculations, topography and roughness studies of the deposited patterns were done via AFM in AC mode on the MFP-3D SA system from Asylum Research Company (USA) with the built-in software based on IgorPro 6.22A.

Utilization of AFM for abovementioned purposes was especially beneficial due to the fact that AFM’s tip is able to sense peculiarities of uneven surface with extreme precision, thus, facilitating high-accuracy yield and roughness calculations along with advanced 3D image rendering (see Figures 2.4, 2.5 (right) and 2.7).

Additionally, the fact that the microscope, used in these studies, was also equipped with a dedicated heating stage allowed us to perform the in-situ AFM
analysis at elevated temperatures, in the range of 21 – 300 °C (as will be discussed later in Chapter 4.3.2 for the case of Au EBID structures analysis).

3.3. Analysis of Functional Properties

3.3.1. Magnetic and magneto-transport studies

For the characterization of Co EBID structures magnetic measurements were carried out by SQUID magnetometer (MPMS2, Quantum Design, USA) and magnetotransport studies were conducted using PPMS (Quantum Design, USA), as will be described later in Chapter 4.2.2.

3.3.2. Electrical measurements

For the electrical properties studies of the SiO\(_{(2+\delta)}\) EBID material, two types of metal-insulator-metal sandwich-like structures were patterned:

1) 4 µm wide Au-Ti lithographically-fabricated bottom electrode covered with 100 nm thick SiO\(_{(2+\delta)}\) intermediate EBID layer and a top 1 µm wide Co EBID electrode, thus, resulting in a tested junction area of 4 \(\times\) 1 µm\(^2\) and a length of 100 nm for the current pathway through the insulator.

2) 1 µm wide Co EBID bottom and top electrodes with 150 nm thick SiO\(_{(2+\delta)}\) intermediate EBID layer, thus, resulting in a tested area of 1 \(\times\) 1 µm\(^2\) and a length of 150 nm for the current pathway through the insulator.

In both cases relatively large SiO\(_{(2+\delta)}\) pads were deposited at 5 kV, 6.3 nA, 6 \(\times\) 11 µm\(^2\) and 3 \(\times\) 10 µm\(^2\) for geometry 1 and 2 respectively. The resistivity of the SiO\(_{(2+\delta)}\) was determined by measurements of the current-voltage characteristics of these devices with applied voltages of both polarities from 0.01 V to 0.3 V. To determine the resistivity the current was measured at each applied voltage with a current to voltage circuit in series with the applied voltage. From the current-voltage relationship and the geometry of the patterned structures the resistivity of the SiO\(_{(2+\delta)}\) was calculated (see Chapter 4.4.3).

3.3.3. Optical properties’ characterization of insulating EBID patterns

The patterned SiO\(_{(2+\delta)}\) were characterized in a Woollam M-2000 ellipsometer (WOOLLAM Inc, USA), which monitors phase-polarization properties of light
reflected from a thin film in order to determine its optical parameters. The 
polarization state of light incident on a sample may be decomposed into s and p 
components (the s and p components correspond to oscillations of electric field 
perpendicular and parallel to the plane of incidence, respectively). After the reflection, 
the normalized amplitudes of the s and p components are denoted as \( r_s \) and \( r_p \), 
respectively. The ellipsometer measures the complex reflectance ratio \( \rho \), which is the 
ratio of \( r_p \) over \( r_s \) and consists of amplitude and phase components:

\[
\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}
\]  

where \( \tan(\Psi) \) is the ratio of \( r_p \) and \( r_s \) amplitudes upon reflection, and \( \Delta \) is the 
phase shift (difference of phases of \( r_p \) and \( r_s \) components). Measured parameters can 
then be substituted into Woollam CompleteEase software, which is capable of 
simulating, with a high precision, of the refractive index \( n \) and the absorption 
coefficient \( k \), using an advanced dispersion model.

In our experiments, we examined rectangular 100 × 50 µm\(^2\) stripes of 50 nm thick 
SiO\(_{2+\delta}\) films deposited on the top of a Si wafer at 5 kV, 6.3 nA. Ellipsometric 
parameters \( \Psi \) and \( \Delta \) were measured under the reflection of white light from an arc 
lamp source with a spectrum ranging from 250 and 1700 nm from the films at various 
angles (from 30 to 60 degrees). The diameter of white light spot on the sample was 
30 µm. The obtained data was then processed in the CompleteEase software and 
compared with optical dispersion curves of conventional silica glasses (see 
Chapter 4.4.2).

### 3.4. Complementary Pre- and Post-Processing Techniques

#### 3.4.1. Buffer layers deposition via PLD method

For the shape control Au EBID studies, buffer layers were deposited on Si 
substrates via Pulsed Laser Deposition (PLD). For PLD a Continuum (model 
NY81-C) Nd: YAG laser operating at \( \lambda = 355 \) nm and 2 mJ/pulse with a pulse 
repetition rate of 10 Hz and energy density of 1.0 J/cm\(^2\) was used. As a material for 
deposition a Si substrate with native oxide surface layer was used. Depositions of the 
Ta/Cr layers were done during 1 min at room temperature (RT) in vacuum. This 
resulted in a 20 nm thickness of the respective Cr and Ta layers, as measured via FIB
section analysis. The topography of the obtained buffer films was uniform and smooth with average root-mean-square (RMS) roughness of 0.5 nm, as measured with an AFM (see Figure 3.4 and Chapter 4.3).

![AFM analysis of Ta and Cr buffer layers](image)

**Figure 3.4.** AFM analysis of (a, b) Ta and (c, d) Cr buffer layers with (a, c) being before and (b, d) after annealing. The Z scale is the same for all the images [16].

3.4.2. *Heat treatment of as-deposited EBID structures*

In the case of EBID from Me$_2$Au(acac) precursor, purification of prototyped patterns was done via post-deposition annealing in ambient and controlled atmosphere, namely air and oxygen. The temperature of heat treatment was varied between 250 – 600 °C to study its effect on the deposit’s chemical composition, as well as to perform precise shape control of annealed structures. Contribution of annealing duration and heating rates were also investigated, including the speed of 0.42 °C/s and 1.26 °C/s.
Experiments were conducted in a micro-furnace TTM-002 (Nitto Kagaku, Japan) and an infrared lamp heating system MILA-5000 (ULVAC-RIKO, Japan), with a well-controlled heating rate (see Chapter 4.3).

3.4.3. Cleanup wet etching

Etching of as-deposited and annealed Au EBID patterns on Ta buffer was carried out in 10% NaOH + 10% H₂O₂ solution for 15 s in the temperature range of 65 – 70 °C. The etching parameters were calculated based on the measured thickness of the buffer layer (see Chapter 4.3).
CHAPTER 4: RESULTS AND DISCUSSIONS

4.1. Aspects of EBIDs’ Purity Enhancement via Deposition at Elevated Temperatures of W-, Si-, Pt-, Co-, and Au-based precursors

The need for pure patterned materials with designated physical properties (e.g. transport, optical or magnetic), is these days a basic requirement for modern nanotechnology fields, such as e.g. microelectronics, plasmonics, biotechnology, etc. Currently EBID is one of the most promising methods for the direct-write mask-less site-specific 3D fabrication of the nanostructures under the abovementioned requirements. However, besides all benefits of this cutting-edge technique, it still has some drawbacks, in particular, low purity of as-deposited materials, due to organometallic nature of precursors applied for patterning and limited dissociation efficiency of the electron beam alone. A number of approaches to enhance chemical composition of prototyped structures was presented in Chapter 2.6. Usually selection of purification approach is strongly based on the chosen precursor.

Frequently, positive purification dynamics is observed after a post-deposition annealing in air or in controlled atmosphere (e.g. O₂, H₂) [4, 9, 16, 19, 20, 35]. However, usually this method also leads to an undesirable shape loss of as-deposited geometries and their reconfiguration due to coalescence processes that occur in nanocrystalline structures during heat treatment step [16, 40]. As an alternative, carbon-free precursors (e.g. Pt(PF₃)₄, WF₆ and etc.) can be used as well [9, 33, 114–117]. They are capable of increasing percentage of metallic component in a deposit more than 3 times, as compared to organometallic gas chemistries. However, large amount of released fluorine contained in a precursor’s molecule is very harmful to samples and microscope’s chamber, causing their uncontrolled etching [115]. Thus, the main focus in this work is on the standard organometallic precursors and challenging optimization of their deposition process. Primarily **EBID onto preheated substrate** is discussed in this sub-chapter, as one of the tested purification strategies.

Among the examined precursors for this approach were MeCpPtMe₃, W(CO)₆, TEOS (tetraethylorthosilicate) and Me₂Au(acac), Co₂(CO)₈, Co(CO)₃NO for the patterning of Pt, W, SiO₂, Au, and Co respectively. The substrate temperature for deposition was ranged from 25 °C to 360 °C. Depending on the value of the
precursor’s spontaneous decomposition temperature (where one is known), above this temperature EBID was generally replaced by a thin film formation with simultaneous loss of prototyping selectivity, as shown in Figure 4.1, left.

In particular, example in Figure 4.1 (left) is given for the case of oxygen assisted spontaneous decomposition of methyl cyclopentadienyl platinum trimethyl (MeCpPtMe$_3$). As known, this precursor is one of the most commonly used for Pt EBID. Its application has been already widely described in literature for creation of suspended nanostructures (SNS) [12], diode-like devices [13], Pt-based nanowires [9, 30, 35, 37, 73, 75, 76] and field emitter prototypes [93, 94, 96–101]. However, as majority of organometallic EBID gas chemistries, deposition from MeCpPtMe$_3$ results in relatively low purity of as-grown material: only around 16 at.% of Pt, rest being carbon. Such behavior significantly affects functional properties of patterned material and leads to considerably larger resistivity than that of pure, bulk Pt [4], independently on the electron beam parameters chosen for deposition.

![Figure 4.1. (Left) SEM image of spontaneous decomposition of the MeCpPtMe$_3$ precursor at 360 °C, in the overlap area of the platinum precursor and the oxygen supply (white area). Without oxygen the precursor does not decompose at this temperature [8]. (Right) Composition of EBID deposition with MeCpPtMe$_3$ as a function of the substrate temperature [8].](image)

In current studies an attempt to increase amount of the metallic content in deposits from MeCpPtMe$_3$ precursor was done via EBID onto a preheated substrate, elevating deposition temperatures from the standard room temperature set point
(25 °C) up to the maximum temperature achievable by our home-built heater – 360 °C [8]. As a result no purity enhancement was observed, keeping Pt concentration in the range of 15 – 20 at.% (Figure 4.1, right), and moreover spontaneous decomposition of this precursor was observed only after performing oxygen-assisted Pt EBID at 360 °C (Figure 4.1, left), indicating that the cyclopentadienyl ring is a very stable molecular group. As well, it is necessary to note that at such high temperature deposition rate was very low, hence any residual carbon contamination could be a competing process.

A different situation was observed for tungsten hexacarbonyl \((W(CO)_6)\) precursor. Even though spontaneous decomposition of this precursor was not achieved up to 360 °C and considerable deposition rate drop was observed at 300 °C and above, significant purity improvement was detected, especially in the range of 25 – 150 °C: from around 35 at.% of W up to almost 60 at.% of W, rest being C and O (Figure 4.2, left). However, at temperatures higher than 150 °C, oxygen content increases, at the cost of a lower W content, suggesting the onset of a partial oxidation process of the deposited W. Four measurements around the peak at 150 °C were repeated more than once to confirm that the peak really exists.

**Figure 4.2.** Graphical representation of dependence between substrate temperature for deposition and chemical composition of EBID structures grown from: \((Left)\) \(W(CO)_6\) and \((Right)\) TEOS precursors with and without additional water vapour supply [8].

For depositions using **TEOS** two sets of curves were recorded: one with TEOS gas molecules only and one with additional mixing of some water vapour, since this combination is often used in conventional chemical synthesis and thus is often
integrated into instrumentation and available to many users [12, 19, 28–30]. Its own EBID from TEOS precursor at elevated substrate temperatures did not lead to purity enhancement, while water-assisted deposition resulted in a slight C content drop from 38 at.\% at room temperature to 32 at.\% at 120 °C (Figure 4.2, right), indicating that water vapor molecules lower the threshold for decomposition. The spontaneous decomposition of TEOS precursor was not observed in this temperature range, which is in agreement with literature where a temperature of 430 °C is reported [118].

When increasing the temperature of the sample, the yield could go either up (due to the increased surface diffusion) or down (due to the lower sticking coefficient). In the case of deposition from TEOS precursor yield decay with a factor of 2.9 was observed: from $8.4 \times 10^{-3} \, \mu m^3 \, nc^{-1}$ after deposition at 25 °C down to $2.9 \times 10^{-3} \, \mu m^3 \, nc^{-1}$ – at 120 °C. This data was in line with a drop of 2.3 reported for SiO$_2$ single pillar growth in the smaller temperature range 25 – 70 °C [119].

For dimethyl gold acetylacetonate $Me_2Au(acac)$ precursor, the measurements were performed using two different Dual Beam microscopes Nova 600 NanoLab: one located at KTH (Sweden), another – at FEI (The Netherlands), to check data reproducibility. In both cases there was a slight purity increase towards higher temperatures (Figure 4.3, left), which is in-line with previous reports [35].

Spontaneous decomposition of the precursor was observed at $\approx 130$ °C, however, it did not result a formation of pure gold film; it still contained $\approx 65$ at\% of carbon. It is suggested that in the low temperature regime (< 100 °C), the precursor loses 2 CH$_3$ groups while at higher temperature the acetylacetonate ring is only partially decomposed, leading to a reduction of the oxygen content. In addition it is confirmed that the higher beam currents produce a slightly higher Au content. Deposition yield of structures grown from $Me_2Au(acac)$ precursor is quantitatively given in Figure 4.3 (right) as a function of patterning temperature. It should be noted that apart from Co precursors, the other gas chemistries, mentioned above, have similar behavior, however, for W(CO)$_6$ and MeCpPtMe$_3$ precursors the lowest values at the end of the temperature scale start to become impractical. The behavior shown in Figure 4.3 (right) is similar to that reported for SiO$_2$ single pillar growth using TEOS precursor in the temperature range of 23 – 70 °C, as reported in [119].
EBID of Co was not as trivial as patterning of other precursors, described above. First of all two different gas chemistries for Co nanoprototyping were investigated: \(\text{Co(CO)}_3\text{NO}\) and \(\text{Co}_2\text{(CO)}_8\), the last one was studied in two different microscopes, as well. Experimentally it was observed that both precursors demonstrate rather special behavior in certain temperature intervals, such as: 100 % EBID, EBID seeded or catalytic growth and spontaneous decomposition, as described in Table 4.1.

The most interesting among those regimes is a short transition segment of the catalytic growth. Comparatively to regular EBID, during this stage growth of Co occurs in all directions, as well as sideways (Figure 4.4). Moreover, deposition rate appears to be \(\cong 50\) times higher and keeps going even when E-beam is no longer present. It stops only when precursor’s gas flow is interrupted.

Analysis of chemical composition shows that deposition from \(\text{Co}_2\text{(CO)}_8\) precursor at elevated temperatures is leading to a significant purity improvement: from \(\cong 55\) at.\% of Co up to more than \(85\) at.\% of Co, the rest being C and O; while EBID from \(\text{Co(CO)}_3\text{NO}\) precursor results only in \(\cong 50\) at.\% of Co, which corresponds to stripping of CO groups, but persistence of the NO group (Figure 4.5). Moreover, for purification of \(\text{Co(CO)}_3\text{NO}\) almost two times higher temperatures are required, as compared to \(\text{Co}_2\text{(CO)}_8\); and concentration of the metallic constituent in spontaneously

**Figure 4.3.** (Left) Composition of EBID deposition with \(\text{Me}_2\text{Au(acac)}\) as a function of substrate temperature [8]. (Right) Yield of the deposition process (at 5 kV, 1.6 nA) using \(\text{Me}_2\text{Au(acac)}\) as a function of the substrate temperature. At temperatures > 120 °C spontaneous decomposition of the precursor starts [8].
decomposed films from Co(CO)$_3$NO precursor is almost twice lower than in the case of patterning from Co$_2$(CO)$_8$ precursor.

**Table 4.1.** Temperature regimes of two cobalt precursors. In each regime the dominant process is different. The EBID seeded growth is a transition regime between pure EBID and full CVD with complete loss of patterning capability.

<table>
<thead>
<tr>
<th>Process</th>
<th>Growth rate</th>
<th>Selectivity</th>
<th>Temperature range Co$_2$(CO)$_8$ ($^\circ$C)</th>
<th>Temperature range Co(CO)$_3$NO ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% EBID</td>
<td>Low</td>
<td>Very good</td>
<td>25 – 55</td>
<td>25 – 120</td>
</tr>
<tr>
<td>EBID seeded growth</td>
<td>High</td>
<td>Omni-directional on seeds only</td>
<td>55 – 65</td>
<td>120 – 130</td>
</tr>
<tr>
<td>Spontaneous decomposition</td>
<td>High</td>
<td>Completely lost</td>
<td>&gt; 65</td>
<td>&gt; 130</td>
</tr>
</tbody>
</table>

**Figure 4.4.** Seeded growth from Co(CO)$_3$NO at 130 $^\circ$C. The growth rate at the beam position is still quite high, but the growth at the substrate background also has started (spontaneous decomposition, not driven by the electron beam) [8].

To summarize this chapter, it is obvious that thermally assisted electron-beam-induced deposition leads to purity improvement of nanoscale depositions for many beam chemistries, maintaining their shape intact. Overall enhancement of chemical composition is achieved at the cost of lower deposition yield, when no seeded growth occurs, as in the case with cobalt patterning. Amount of improvement is different for
each precursor. Within the maximum temperature range of 360 °C, the best factor of enhancement was found for W(CO)$_6$ precursor: from 36.7 at.% at 25 °C to 59.2 at% at 280 °C. For Co(CO)$_3$NO and Me$_2$Au(acac) precursors only slight improvement was observed, while deposition at elevated temperatures from MeCpPtMe$_3$ and TEOS precursors did not result in any enhancement; however, marginal improvement was observed in the case of water-assisted TEOS EBID. Thus, for Me$_2$Au(acac) gas chemistry it is recommended to try out post-deposition annealing, for TEOS – intermixing with oxygen that my lead to reactive burn off of residual carbon, and in the case of rather promising Co nano-prototyping, focus most likely should be done on Co$_2$(CO)$_8$ precursor and further optimization of its deposition parameters at elevated temperature, as will be discussed in Chapter 4.2.

![Figure 4.5](image)

**Figure 4.5.** *(Left)* Composition of EBID depositions with Co(CO)$_3$NO as a function of the substrate temperature. In the range 120 – 130 °C structures are created by seeded growth at high rate. Above 130 °C the composition is the result of the spontaneous decomposition process [8]. *(Right)* Composition of EBID deposition with Co$_2$(CO)$_8$ as a function of the substrate temperature. The measurements were done on two different microscopes, denoted on the graph as System 1 and System 2 [8].
4.2. Nano- to Micro-Scale Patterning of Pure Cobalt

4.2.1. Combination of EBID and seeded growth at elevated temperatures from Co$_2$(CO)$_8$ precursor

As discussed in Chapter 4.1, thermally-assisted EBID appears to be a rather promising method for purification of nano- to micro-scale structures grown from Co$_2$(CO)$_8$ precursor. Moreover, this process leads to significant deposition yield enhancement of Co patterned structures via possible utilization of seeded growth approach, while for majority of other gas chemistries EBID at elevated temperatures results in dramatic deposition rate drop.

In order to get proper understanding of electron-beam-assisted seeded growth of Co, further systematic studies of this deposition process were required in a combination with subsequent functional properties analysis of nanoprototyped material, in particular its magnetic and transport characteristics.

First of all, it was observed that EBID from Co$_2$(CO)$_8$ precursor is rather sensitive to vacuum conditions (see Table 3.1), as well as beam energy and intensity, used for deposition, both at elevated and room temperatures (Table 4.2, Figure 4.6).

![Figure 4.6. Typical EDXS spectra for (a) room temperature (57 at.% Co) and (b) 70 °C EBID (> 98 at% Co) [22].](image-url)
Then the higher was current, the better was purity of as-deposited material. In particular, 100% pure Co structures were formed via EBID at 60 °C, using 2 kV, 3.4 nA for deposition, while patterning at the same substrate temperature, but utilizing 5 kV, 1.6 nA, resulted only in 82.4 at.% of Co, rest being C and O.

Fine structure evaluation of Co EBID materials deposited at different substrate temperatures was done via HR TEM analysis. In the cases of patterning at room temperature and 60 °C, formation of a somewhat similar polycrystalline structure was observed, with nanocrystallites being on an average ≅ 1 nm larger at 60 °C EBID than at RT deposition (Figure 4.7).

Table 4.2. Compositions of EBID deposits obtained at different substrate temperatures with two different beam settings.

<table>
<thead>
<tr>
<th>Substrate temperature, °C</th>
<th>Deposition at 5 kV, 1.6 nA</th>
<th>Deposition at 2 kV, 3.4 nA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co (at.%)</td>
<td>C (at.%)</td>
</tr>
<tr>
<td>24</td>
<td>57.5</td>
<td>22.0</td>
</tr>
<tr>
<td>50</td>
<td>76.6</td>
<td>14.0</td>
</tr>
<tr>
<td>60</td>
<td>82.4</td>
<td>11.6</td>
</tr>
<tr>
<td>70</td>
<td>83.2</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Figure 4.7. HR TEM images of Co EBID patterns deposited at (a) room temperature and (b) 60 °C [22].
Further elevation of deposition temperature up to 70–85 °C and higher (depending on vacuum conditions) led to a spontaneous thermal decomposition of the precursor gas molecules on the surface of Si substrate, coating a fairly large area with pure crystalline cobalt (Figure 4.8(a)). At the onset of the decomposition this formed layer consisted of small particles of pure cobalt (Figure 4.8(b)) that further turned into larger faceted Co crystals (Figure 4.8(c)).

Figure 4.8. SEM images of: (a) Spontaneous thermal decomposition over a large area at 75 °C. The arrow indicates the position and direction of the GIS needle. (b) Formation of small Co particles at onset of the decomposition. (c) Large Co crystals formed during ≅5 min exposure of the surface to the Co₂(CO)₈ vapor [22].

As shown from TEM analysis these thermally decomposed faceted crystals have polycrystalline structure (Figure 4.9). They consist of 100 % pure cobalt with no evidence of carbon or oxygen presence in chemical composition, as proven via both EDXS and EELS studies. Moreover, elevation of the substrate temperature significantly increased growth rate of polycrystalline cobalt films.

However, despite all the benefits of such prototyping process at ≅ 70–85 °C, leading to formation of pure crystalline cobalt, this approach has a dramatic drawback – spontaneous decomposition results in the loss of patterning selectivity. On the way towards solving this challenging problem an interesting behaviour of Co₂(CO)₈
precursor was discovered in our lab. If deposition was done slightly below the temperatures of spontaneous thermal decomposition, Co active growth was observed in areas that had prior heavy exposure to the electron beam (like those after EDXS acquisition, prolonged imaging, etc.). Thus, we found that this growth process can be triggered by the deposition of very small amounts of carbon on the surface for patterning. Moreover, it was established that EBID from Co$_2$(CO)$_8$ precursor performed on top of the intentionally deposited carbon areas leads to formation of crystalline cobalt as well even at the patterning temperature below spontaneous thermal decomposition.

![Figure 4.9. Bright field STEM image of cobalt thermally decomposed from Co$_2$(CO)$_8$ on silicon substrate at 75 °C [22].](image)

Required seeded carbon layer can be either grown from commercially available carbon-based precursors or via prolonged e-beam rastering over fabrication area, with no gas chemistry supply, utilizing instead residual hydrocarbons present in the microscope chamber. It is a rather fast process, especially taking into account that only a nanometer or so thin carbon layer is required for catalytic growth of cobalt. Moreover, seeded growth leads to a considerable growth rate enhancement, as compared to regular deposition at elevated temperatures, which results in a dramatic
yield drop. Thus, for instance, at 55 °C, well below the thermal decomposition temperature of Co$_2$(CO)$_8$, EBID over pre-deposited carbon seed of a 50 µm × 2 µm rectangle at 2 kV, 3.4 nA during 30 min produces a 1 µm thick wire of crystalline Co (Figure 4.10), which corresponds to yield of $16.4 \times 10^{-3}$ µm$^3$ nC$^{-1}$. Such excellent growth rate of high-purity cobalt allows fabrication of much larger patterns/areas as well.

![Figure 4.10. SEM images of cobalt wire produced for 4-probe transport measurements on Si$_3$N$_4$ substrate by EBID on carbon seeds. (a) C seed layer produced by 5 min of C EBID [22]. (b) Crystalline Co grown by EBID at 55 °C at 2 kV, 3.4 nA for 30 min (the image is taken with the view at 52° tilt of the stage) [22].](image)

Figure 4.11. SEM images of (a) Cobalt wire produced for Hall probe measurements on Si$_3$N$_4$ substrate by EBID on C EBID seeds at 65 °C at 2 kV, 3.4 nA for 60 min (the image is taken with the view at 52° tilt of the stage) [22]. (b) Seeded Co EBID patterns grown at 70 °C. Seeding layer was produced by rastering e-beam inside the patterns without precursor gas. The arrows indicate two pads grown on rectangular seed patterns versus two circular patterns next to them [22].
Further increase of patterning temperature, closer to spontaneous thermal decomposition values, enhances yield of seeded-grown Co structures even more (e.g. $26.1 \times 10^{-3}$ µm$^3$ nC$^{-1}$ at 65 °C, see Figure 4.11(a)), but at the same time it leads to undesirable shape control difficulties of smaller size patterns, including rounding off artefacts at the corners of designed features (Figure 4.11(b)).

4.2.2. Magnetic and transport properties of the Co EBID and seeded structures

Systematic characterization of Co-patterned structures was started from SQUID magnetometry studies of samples grown at room temperature. For that purpose, 14 square pads (5 µm × 5 µm wide and ≅ 370 nm tall) were deposited at 5 kV, 6.3 nA on a 3 mm diameter piece of purely diamagnetic thin aluminium foil, as was identified with the SQUID prior to deposition. Purity of grown structures was somewhat better than usual (Table 4.2), reaching 81 at.% of Co, 6 at.% of O and 13 at.% of C, most likely due to the local heating induced by the higher beam current during prolonged exposure along with differences in the substrate properties and heat sinking method (related to mounting and the nature of the substrate). As well at the end of deposition a very thin layer of cobalt was also found in the area surrounding the pads, coming probably from snapshots during the deposition (Figure 4.12, left), which made it difficult to estimate total volume of the deposited Co. SQUID results showed that room temperature nanoprototyped Co is a very soft ferromagnetic material with a coercivity close to zero and a remanent magnetization on the order of $0.75M_S$, where $M_S$ is the saturation magnetization (Figure 4.12, right).

The magnetotransport properties of several Co-fabricated samples were further studied using 4-terminal geometry of specimens, as shown in Figure 4.11 (left), to analyse their resistivity, anisotropic magneto-resistance (AMR) and Hall voltage values. It was observed that Co grown on a carbon seed layer clearly has better transport and magnetotransport properties than standard Co EBID. Deposition at 55 °C and above was producing the best quality Co, as described in Table 4.3. Moreover, we found that the deposition temperature of 55 °C seemed to be a sort of threshold between “good” and “bad” Co. Thus, carbon seeded deposition at 58 °C and 65 °C resulted in Co EBID resistivities of 21 and 22 µΩ cm, which is significantly better than the properties of specimens fabricated via standard EBID at 50 °C with beam parameters of 5 kV, 6.3 nA (Table 4.3). These values are, however, larger than
the 6 \( \mu \Omega \) cm value of bulk Co [120], but comparable to 13 \( \mu \Omega \) cm resistivities of thin films found by McGuire and Potter [121]. Since, resistivity depends upon the crystalline quality of the films [122] the trend we observe is further evidence that the films grown with the carbon seed are of higher quality.

![Image](image.png)

**Figure 4.12.** The left-hand image shows overview of the square pads deposited at room temperature on Al foil for SQUID measurements. Area where additional deposition of Co occurred due to snapshots during and between the individual depositions is clearly visible [22]. The right-hand image shows room temperature magnetization loop for the sample with Co EBID. The inset shows the magnified loop with subtracted diamagnetic contribution of the substrate [22].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity ((\mu \Omega ) cm)</th>
<th>Residual resistivity ratio</th>
<th>AMR (%)</th>
<th>( M_S ) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 °C standard EBID</td>
<td>152</td>
<td>1.10</td>
<td>0.02</td>
<td>0.9</td>
</tr>
<tr>
<td>58 °C with carbon seed</td>
<td>22</td>
<td>1.61</td>
<td>1.2</td>
<td>1.25</td>
</tr>
<tr>
<td>65 °C with carbon seed</td>
<td>21.4</td>
<td>1.81</td>
<td>1.2</td>
<td>1.55</td>
</tr>
</tbody>
</table>

The calculated and fitted saturation magnetization value from the Hall effect measurements (Figure 4.13) was estimated as \( 4\pi M_S \), assuming that the sample was a uniform thin film [123]. Obtained \( 4\pi M_S \) values for Co deposited above 55 °C were a bit less than but comparable to those for bulk Co of 1.8 T (Table 4.3).

Thus, we claim that we developed a method for fabrication of high-quality pure crystalline Co via combination of EBID at elevated temperatures and catalytic seeded
growth from Co$_2$(CO)$_8$ precursor. The created nanomaterial has outstanding magnetic and transport properties comparable to values of Co in bulk and thin film states. As well we report that this process results in a significantly faster deposition rate than standard temperature-assisted EBID.

![Graph of Hall voltage vs. magnetic field](image)

**Figure 4.13.** The Hall voltage as a function of magnetic field applied perpendicular to the plane for the sample grown at 65 °C listed in Table 4.3. The current used in the measurement was 1 mA. The large slope around the origin is due to the extraordinary Hall effect and the small slope at high fields the ordinary Hall effect [22].

### 4.3. EBID of Gold from Me$_2$Au(acac) Precursor. Purification and Shape Control

#### 4.3.1. Purification and shape control approaches for creation of planar nanoscale Au structures

Gold is a material of substantial interest for nanotechnological applications, such as e.g. electronics, plasmonics, biotechnology, life sciences and etc. [2, 16, 19, 31, 34, 40, 41, 92, 124]. It can be used for fabrication of field emitter devices, quantum dots, plasmonic nanostructures, nanowires, biosensors and lab-on-chip architectures, to name just a few. However, site-specific nanoscale fabrication of pure gold is rather nontrivial. EBID is one of the methods used for such nanoprototyping. Au-based nanostructures designed via this approach usually contain quite a low amount of
metallic constituent, due to organometallic nature of applied precursors. In particular deposition from one of the most commonly used Au organometallic gas chemistry, Me$_2$Au(acac), usually results in 8 – 12 at. % of Au, rest being C. In our work we focused on this specific precursor and developed the shape-controlled purification routine for Au electron-beam-induced deposition.

Among a variety of existing EBID purification approaches, in this project, effect of ex-situ heat treatment on further chemical composition enhancement and deposits’ shape tailoring was studied. Its selection was based on previously described in Chapter 4.1 results of purification attempts via deposition onto preheated substrate, which led to slight improvement. During experimental process, based on literature survey [4, 9, 35], one more factor was taken into consideration – poor adhesion of gold to glass and silicon substrates, which stimulated rearrangement of Au grains and nanoparticles during the annealing process. Thus, to solve this problem, additional buffer layers were PLD ablated on the Si substrates, utilizing Cr and Ta materials (see Figure 3.4).

Fine structure of as-deposited patterns from Me$_2$Au(acac) precursor consists of 4.8 nm Au nanoparticles embedded into the carbonaceous matrix, as proven by HR TEM analysis and electron diffraction (see Figure 2.8). When ex-situ post-deposition heat treatment is initiated Au nanocrystals start coalescing [40] and forming larger grains, while carbonaceous by-products are pushed towards new grain boundaries, diffused out and gradually burned off, when reaching the top surface of the deposit. But at the same time during annealing of fabricated nanostructures the changes are occurring not only within the Au-based deposits, but also inside the buffer layers. Thus, while Ta keeps its original amorphous continuous shape (Figures 4.14 and 3.4), Cr is undergoing severe structural changes, transforming into crystalline material (Figures 4.15 and 3.4), and, therefore, leading towards coarse crystalline and non-uniform structure formation of annealed Au EBID (Figure 4.16). Such Cr behavior determined our decision to conduct further experiments utilizing Ta buffer layer only, which was facilitating homogeneous fine-granular Au structure formation after heat treatment (Figure 4.17).

Generally annealing was done at 600 °C, for 1 hour in air. Following conditions were experimentally identified as the most suitable for purification of deposits from Me$_2$Au(acac) precursor. As a result, purity of EBID structures improved dramatically,
up to > 92 at.% of Au (Figure 4.18), rest being C trapped in between grain boundaries of large freshly-formed Au crystals (Figure 4.14(b)). Such significant chemical composition enhancement, caused by burning off residual carbonaceous matrix, was at the same time leading to the volume loss of as-deposited structures by a factor of \( \cong 2 \), as was studied with AFM and summarized in Table 4.4.

**Figure 4.14.** TEM BF image of the deposition on the Ta buffer layer

(a) before and (b) after annealing [16].

**Figure 4.15.** TEM BF image of the deposition on the Cr buffer layer

(a) before and (b) after annealing. Both images have the same scale [16].

Meanwhile, it was also observed that the degree to which EBID patterns reconfigure during the annealing step was strongly dependent on the original shape and size of the grown structures, and thus on the e-beam fabrication parameters, such as accelerating voltage, current and pitch size. The best results of fine-granular uniform planar Au nanostructure formation, with RMS of 2.8 nm and average grain
size of $\approx 50$ nm, were achieved after the annealing of dot array (DA) pattern deposited at 5 kV, 6.3 nA, with a slight defocus of 50 nm (Figure 4.19). Most likely such specific reconfiguration dynamics was connected to the fact that substitution of a continuous layer by dots allows for a better controlled and homogeneous nucleation process. Multifold increase in surface area promotes faster carbon diffusion. And the fact that the dots are close to each other combined with the buffer layer, which restricts surface mobility of gold, results in creation of a homogeneous fine-granular layer at the end of annealing.

**Figure 4.16.** AFM analysis of Au EBID pad deposited on Cr buffer at 5 kV, 1.6 nA, $1 \times 1 \mu$m (a) before and (b) after annealing at 600 °C during 1 h in air. The Z scale is the same for both images [16].

**Figure 4.17.** AFM analysis of a pad deposited on Ta buffer at 2 kV, 0.84 nA, $1 \times 1 \mu$m (a) before and (b) after annealing. The Z scale is the same for both images [16].
Table 4.4. Relative volume reduction of Au EBID on Ta buffer as result of annealing depending on pattern type and deposition parameters.

<table>
<thead>
<tr>
<th>Type of pattern</th>
<th>Voltage (kV)</th>
<th>Beam current (nA)</th>
<th>Pattern size (µm)</th>
<th>Deposition time (sec)</th>
<th>Dwell time (µs)</th>
<th>Pitch (nm)</th>
<th>Height before annealing (nm)</th>
<th>Volume before annealing $V_b$ (µm$^3$)</th>
<th>Volume after annealing $V_a$ (µm$^3$)</th>
<th>Relative volume loss $V_l$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pad #1</td>
<td>5</td>
<td>1.6</td>
<td>1×1</td>
<td>60</td>
<td>15</td>
<td>23</td>
<td>70</td>
<td>0.083</td>
<td>0.051</td>
<td>38</td>
</tr>
<tr>
<td>Pad #2</td>
<td>5</td>
<td>6.3</td>
<td>1×1</td>
<td>30</td>
<td>15</td>
<td>46</td>
<td>80</td>
<td>0.098</td>
<td>0.084</td>
<td>14</td>
</tr>
<tr>
<td>Pad #3</td>
<td>2</td>
<td>3.4</td>
<td>1×1</td>
<td>30</td>
<td>15</td>
<td>53</td>
<td>87</td>
<td>0.1</td>
<td>0.077</td>
<td>23</td>
</tr>
<tr>
<td>Pad #4</td>
<td>2</td>
<td>0.84</td>
<td>1×1</td>
<td>60</td>
<td>15</td>
<td>27</td>
<td>80</td>
<td>0.093</td>
<td>0.047</td>
<td>49</td>
</tr>
<tr>
<td>DA$^b$ #1</td>
<td>5</td>
<td>1.6</td>
<td>3×3</td>
<td>120</td>
<td>500</td>
<td>200</td>
<td>67</td>
<td>0.28</td>
<td>0.095</td>
<td>66</td>
</tr>
<tr>
<td>DA #2</td>
<td>5</td>
<td>6.3</td>
<td>3×3</td>
<td>180</td>
<td>500</td>
<td>200</td>
<td>95</td>
<td>0.63</td>
<td>0.29</td>
<td>54</td>
</tr>
<tr>
<td>DA #3</td>
<td>2</td>
<td>0.84</td>
<td>3×3</td>
<td>120</td>
<td>500</td>
<td>200</td>
<td>54</td>
<td>0.28</td>
<td>0.096</td>
<td>66</td>
</tr>
<tr>
<td>DA #4</td>
<td>2</td>
<td>3.4</td>
<td>3×3</td>
<td>180</td>
<td>500</td>
<td>200</td>
<td>81</td>
<td>0.61</td>
<td>0.24</td>
<td>61</td>
</tr>
<tr>
<td>Line #1</td>
<td>20</td>
<td>0.15</td>
<td>10</td>
<td>40</td>
<td>1000</td>
<td>200</td>
<td>62</td>
<td>0.0013</td>
<td>0.00052</td>
<td>60</td>
</tr>
<tr>
<td>Line #2</td>
<td>20</td>
<td>0.15</td>
<td>10</td>
<td>80</td>
<td>2000</td>
<td>200</td>
<td>108</td>
<td>0.0034</td>
<td>0.0023</td>
<td>32</td>
</tr>
<tr>
<td>Line #3</td>
<td>20</td>
<td>0.15</td>
<td>10</td>
<td>120</td>
<td>3000</td>
<td>200</td>
<td>145</td>
<td>0.0056</td>
<td>0.0045</td>
<td>20</td>
</tr>
<tr>
<td>Line #4</td>
<td>5</td>
<td>1.6</td>
<td>10</td>
<td>30</td>
<td>15</td>
<td>23</td>
<td>67</td>
<td>0.0068</td>
<td>0.0023</td>
<td>66</td>
</tr>
<tr>
<td>Line #5</td>
<td>5</td>
<td>1.6</td>
<td>10</td>
<td>31</td>
<td>15</td>
<td>100</td>
<td>120</td>
<td>0.012</td>
<td>0.005</td>
<td>58</td>
</tr>
<tr>
<td>Line #6</td>
<td>5</td>
<td>1.6</td>
<td>10</td>
<td>20</td>
<td>500</td>
<td>200</td>
<td>73</td>
<td>0.0039</td>
<td>0.0012</td>
<td>69</td>
</tr>
</tbody>
</table>

$^aV_l = (V_b - V_a) / V_b \times 100%.$ $^bDA = dot array.$

Thus, by additional manipulation of deposition parameters, it was possible to move on from patterning of planar continuous Au structures and to achieve fabrication of site-specifically localized individual nanoscale Au dots, with large enough distance between them, via heat treatment of lines consisting of dots deposited at 5 kV, 1.6 nA with a 200 nm pitch (Figure 4.20).
Figure 4.18. Typical EDXS spectra acquired in TEM for (a) as-deposited EBID and (b) within a grain of the annealed Au EBID pad on a buffer layer. The Cu signal is a result of the primary scattering in the TEM grid, not related to EBID structures [16].

Figure 4.19. AFM analysis of a dot array deposited at 5 kV, 6.3 nA, 3 × 3 µm (a) before and (b) after annealing. (Inset) detailed morphology after annealing. The Z scale is the same for image (a) and (b) [16].
4.3.2. Tailoring of deposition vs. annealing conditions to form high aspect ratio periodic Au nanopatterns

Even though significant level of breakthrough was attained in the area of nanoprototyping of planar Au EBID structures, it was still challenging to grow complicated 3D Au nanostructures, due to shape distortion problems occurring during heat treatment process. Thus, it was realized that systematic analysis of dependencies between as-deposited shape and size, purification parameters and final structure formation is strongly needed.

For the initial studies a so-called the height to area (HAR) factor was taken into account and 3 kinds of block type patterns were analyzed with HAR parameters shown in table 4.5 and calculated according to equation (4.1), where h is height and A is area.

\[
HAR = \frac{h}{A} \times 100\% \quad (4.1)
\]

As it was observed after series of AFM scans at elevated temperatures (22, 50, 100, 150, 200, 220, 240, 260, 280 and 300 °C), the primary height changes of as-deposited structures were taking place at the temperature of 240 °C (Figure 4.21, top). The significant factor of 2 height drop for the samples with 1.9 and 12 %/µm HAR value and a factor of 3 height drop for the samples with 46 %/µm HAR were observed after the subsequent gradual temperature increases up to 300 °C.
Table 4.5. Characteristics of 3 different HAR Au EBID patterns grown at 5 kV, 1.6 nA.

<table>
<thead>
<tr>
<th>Height to area ratio (%/µm)</th>
<th>Pattern size (µm)</th>
<th>As-deposited height (nm)</th>
<th>Deposition time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>1.5 × 1.5</td>
<td>1042</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>1 × 1</td>
<td>123</td>
<td>1</td>
</tr>
<tr>
<td>1.9</td>
<td>3 × 3</td>
<td>170</td>
<td>10</td>
</tr>
</tbody>
</table>

It was concluded that in order to obtain densely-packed fine-granular uniform structure after annealing at 300 °C and/or 600 °C the structures with lower HAR factor should be used, such as 1 – 2 %/µm (Figures 4.22(f) and 4.23(b)), since patterns with higher HAR values usually transform into coarse-granular (Figures 4.22(e) and 4.23(a)) or even agglomerated structures (Figure 4.22(d)).

The annealing temperatures of 300 – 400 °C were considered to be a somewhat critical points in a heat treatment purification procedure, because already at that moment majority of carbonaceous matrix in Au EBID patterns was burned off, leading to Au concentration improvement up to 60 and 70 at.% respectively, as confirmed by a dedicated EDXS analysis (see Figure 4.21 (bottom)).

This phenomenon inspired us to apply following purification routine to 3D nanostructures, in particular high-aspect ratio pillar arrays deposited at 18 kV, 0.15 nA and a 150 nm pitch, which usually collapse and completely lose their shape after heat treatment at 600 °C. The initial annealing at 250 °C for 1 h of 500 nm tall nanocrystalline pillars, with bottom diameter of 70 nm and top diameter of η 10 nm, (Figure 4.24(a)), showed that already at this temperature Au nanoparticles start coalescing (Figure 4.24(b)), which was in-line with the observations about beginning of the height loss at 240 °C, discussed previously in Figure 4.21 (top). Subsequent temperature increase up to 300 °C resulted in formation of a more coarse-granular gold structure with the presence of a residual carbonaceous part in it that served as an intermediate agent between isolated Au grains in separate cases (Figure 4.24(c)).

Further elevation of heat treatment temperature up to 400 °C and reduction of the annealing duration down to 30 min, that was expected to burn off residual carbon trapped in matrix, unfortunately led to irreversible changes and original high aspect ratio loss of pillars transforming them into blobs (Figure 4.24(d)).
Figure 4.21. Graphical representation of the effect of post-annealing temperature on (top) the height changes of as-deposited Me$_2$Au(acac) pads of 3 different height to area ratios: 1.9, 12 and 46 %/µm (observations and calculations were performed during the AFM analysis at elevated temperatures); (bottom) the chemical composition changes of as-grown Au-containing pads [36].

The solution of this severe post-annealing restructuration problem was found via heating rate increase, minimizing the coalescence time for the gold nanoparticles, and performing heat treatment in the presence of O$_2$ that speeds up oxidation process in carbon present in the deposits, as suggested in [9]. Thus, following oxygen-assisted annealing at 400 °C for 30 min, with the heating rate of 1.26 °C/sec, led to formation of well-aligned 150 nm tall, and 50 nm wide diameter at the base, pillar arrays with
the fine-granular Au structure (see Figures 4.24(e) and 4.24(f)), opening the door towards site-specific 3D Au nanofabrication.

![AFM images](image)

**Figure 4.22.** AFM images (3D representation) of (a – c) as-deposited and (d – f) annealed pads at 300 °C directly on the AFM heating stage. Patterns with 3 different height to area ratios were studied: (a, d) 46 %/µm, (b, e) 12 %/µm and (c, f) 1.9 %/µm. The Z scale is the same for the following pairs of images: (a) and (d), (b) and (e), (c) and (f), and is represented to their left side [36].

4.3.3. *Cleanup wet etching step for further device application*

Application of Ta buffer layer is indeed one of the key factors in shape-controlled purification process of Au EBID nanostructures due to its outstanding wetting properties [16, 125]. However, frequently for device applications it is strongly undesirable to have a continuous metallic layer on the substrate. Thus, to remove the buffer layer after deposition and annealing on those areas that have not been patterned we used an etching approach, reported in [126]. Taking into account the 20 nm thickness of Ta buffer, the following etching parameters were experimentally considered to be the most successful:

1) 10% NaOH + 10% H₂O₂ solution;
2) Etching temperature range of 65 – 70 °C;
3) Etching duration of 15 s;

4) Active washing of sample 2 times in hot DI water (55 – 60 °C) during 5 min;

5) Optional sonication in hot DI water (55 – 60 °C) during 5 min.

It was observed that Ta layer can be completely removed from the areas not covered by EBID, without affecting the gold patterns, as proven both via FIB cross-section (Figure 4.25) and AFM analysis (Figure 4.26).

![AFM images](image)

**Figure 4.23.** AFM images (3D representation) of the central top part of the post-annealed pads for 1 h at 600 °C in air. (a) Nanostructure of the pad with the height to area ratio of 12 %/µm and (b) 1.9 %/µm. The Z scale is the same for both images [36].

Moreover, it was established that the etching procedure can be performed either before (Figures 4.25–4.26) or after the annealing (Figure 4.27). However, the best results were obtained for etching done before the annealing (Figure 4.25(b)). In the case of post-annealing etching undesirable etching can occur at the grain boundaries and between the grains of the crystalline gold (Figure 4.27(b)).

Thus, it was confirmed that the post-deposition annealing is a very efficient purification method for Au EBID structures, leading to a dramatic purity improvement and allowing nanofabrication of both planar and 3D Au nanostructures, when thorough consideration of HAR factor, heat treatment parameters and recommended Ta buffer application is done.
Figure 4.24. SEM images, acquired at a 52° tilt, representing the nanostructure of (a) as-deposited pillar array at 18 kV, 0.15 nA, where (Inset) shows the HR TEM image with the fine structure of 1 pillar; (b – f) pillar arrays annealed at different conditions: (b) 250 °C, 1 h, in air, with the heating rate of 0.42 °C/sec, (c) 300 °C, 1 h, in air, with the heating rate of 0.42 °C/sec, (d) 400 °C, 30 min, in air, with the heating rate of 0.42 °C/sec, (e, f) 400 °C, 30 min, in oxygen presence, with the heating rate of 1.26 °C/sec, where (e) is the zoomed central part of the annealed pillar array shown in (f) [36].

Figure 4.25. SEM images of as-deposited Au EBID: (a) FIB cross-section analysis of as-deposited pad after etching procedure, with the view at a 52° tilt; (b) morphology after etching and subsequent annealing [16].
Figure 4.26. AFM section analysis of the same Au pad before and after etching [16].

Figure 4.27. SEM images of Au EBID after post-annealing etching procedure: (a) FIB cross-section, with the view at a 52° tilt; (b) top view (areas where gold peeled off from the Ta buffer layer are marked with arrows) [16].

4.4. Nanopatterning of Si-Based Insulating Materials via Gas-Assisted EBID

4.4.1. Oxygen-assisted EBID from TEOS precursor: challenges and discoveries

Over the past years a number of different chemical composition enhancement steps were applied to the charged-particle fabrication of SiO₂ from TEOS precursor, including focused ion-beam-induced deposition (IBID) [42–44], post-annealing of the EBID structures [20], deposition on a preheated substrate [8], water- [8, 12, 29, 30] and oxygen-assisted EBID [23–27]. Among all listed above approaches only the last
one was giving a significant improvement and formation of carbon-free SiO$_2$, with no side effects, such as e.g. Ga$^+$ ions implantation in the case of IBID. However, besides all benefits, this method had certain constrains as well. So, in order to supply simultaneously second gas (oxygen) into a microscope’s chamber, apart from TEOS precursor gas molecules, additional second needle was required for utilization. This condition was involving certain level of exploitation complexity and application range limitations of prototyped SiO$_2$, especially for design of complicated 3D geometries with high-angular patterning tilts [12, 28, 29, 65, 101].

In our work we developed a method allowing application of a single needle for intermixing of TEOS and oxygen directly inside it (Figure 4.28(b)). Such approach besides leading towards pure SiO$_2$ deposition, as well significantly eased up handling and alignment procedure.

For both supply methods it was observed that the crucial parameter in this purification step is the amount of oxygen gas, co-introduced into the chamber during deposition process. Thus, experimentally it was established that at the base pressure of $\approx 1 \times 10^{-6}$ mbar the minimum total pressure of $\approx 5.5 \times 10^{-5}$ mbar should be utilized for deposition of SiO$_2$, containing about 2 at.% of C; and for the absolutely carbon-free oxide prototyping total pressure should be on the order of $\approx 7 \times 10^{-5}$ mbar (see Figure 4.29). Going above this level of total working pressure does not lead to any further changes in the chemical composition of the deposited structures, which is consistent.
with that found previously [24]. The Si and O₂ contents in deposited structures were determined using EDXS in both SEM and TEM. It was observed that oxygen to silicon ratio was not perfectly stoichiometric and varied from 1.96 to 2.28, thus, resulting in the formula of SiO\textsubscript{(2+δ)}, where δ diverged from −0.04 to +0.28.

![Figure 4.29. Typical EDXS spectrum acquired in SEM for the EBID pad grown from TEOS precursor at 5 kV, 6.3 nA in the oxygen atmosphere at the working pressure of \( \approx 7 \times 10^{-5} \) mbar. No peak at the carbon Kα line at 0.2774 keV is detected.](image)

So, considering that primary analysis of chemical composition and fine structure of deposits, done utilizing both 2-needles and single needle approaches showed similar EDXS results (Figure 4.29) along with identical structural details proving amorphous nature of patterned material (Figures 4.30 and 4.31) in both cases, it was decided that further characterization of physical functional properties should be performed using the developed single-needle approach due to its simplicity.

### 4.4.2. Studies of optical properties

To study optical characteristics of the deposited Si-based films, the ellipsometry method was used. The spectral dependences of two main ellipsometric parameters (Ψ and Δ) under the reflection of white light from a 50 nm thick SiO\textsubscript{(2+δ)} pad deposited on top of Si substrate are shown in Figure 4.32(a). Even though slight stoichiometric deviations were observed during EDXS analysis, the optical data presents good correspondence to the similar parameters for fused SiO\textsubscript{2} taken from classical Palik’s handbook on optical constants [127]. This experimental fact evidenced the similarity of optical characteristics (transparency, absorption \( k_\lambda \), and refractive index n) within a
wide wavelength range between 250 and 1700 nm. Further raw ellipsometric data correction, with increased measurements precision, showed that the closest approximation of absorption coefficient $k_\lambda$ occurs when it is around zero ($k_\lambda < 10^{-6}$), which is in-line with previous data on SiO$_2$ films. The results of refractive index $n(\lambda)$ analysis are presented in Figure 4.32(b). It was observed that $n(\lambda)$ varies from 1.5 to 1.47 for the wavelengths between 400 and 1700 nm, having $n = 1.48$ in the center of the visible range. Comparative analysis to the several industrially important glasses, including fused silica film [127], crystalline quartz [127], 7059 glass and BK7 from Schott [128] (Figure 4.32(b)) showed that patterned SiO$_{(2+\delta)}$ material is similar to amorphous silica with oxidization of SiO$_x$ being very close to $x = 2$. Such combination of measured optical properties gave us indirect evidence that we are dealing with excellent insulator.

Figure 4.30. HR TEM images of the SiO$_{(2+\delta)}$ EBID created via co-deposition approach. Cross-sectional view of (a) the top part of 100 nm thick pad, deposited at 5 kV, 1.6 nA; (Inset) represents its FFT that indicates amorphous structure of the pad; (b) $\approx$ 3 nm thin continuous layer, deposited at 5 kV, 0.4 nA.

4.4.3. Electrical measurements of the SiO$_{(2+\delta)}$ EBID-grown material

Electrical transport investigation of the SiO$_{(2+\delta)}$ EBID-grown material were performed on 4 samples with 2 different specimen geometries, described in Chapter 3.3.2. In total 35 measurements within voltage range between ±0.01V and ±0.3V resulted in an average resistivity of $\rho = 7.25 \text{ G}\Omega \text{ cm} \pm 4.65 \text{ G}\Omega \text{ cm}$. The measured
resistivities were independent of the bias voltage, indicating ohmic behavior over the analyzed range and the sample to sample variation within a factor of 1.9. Moreover, obtained resistivity values for patterned material were about 2 orders of magnitude larger than those of silicon dioxide grown via IBID from TEOS precursor [43], most likely pointing out the effect of undesirable Ga$^+$ ions implantation and residual C atoms presence in the IBID prepared materials.

**Figure 4.31.** HR TEM images of the SiO$_{(2+\delta)}$ pillars deposited directly on the edge of the Cu TEM grid at 5 kV, 0.4 nA for 5, 10 and 20 s respectively via the single-needle intermixing approach. (a) Overview of the grown pillars, (Inset) shows fine structure of the tallest pillar’s tip; (b, c) zoomed images of the tip of the shortest pillar; (d) selected area electron diffraction pattern acquired at the tip of the shortest pillar, indicating amorphous structure of the oxide.
Figure 4.32. (a) Spectral dependence of ellipsometric data Ψ (red curve) and Δ (green curve) obtained under 60-degree reflection from patterned SiO$_{2+δ}$ films. Dotted lines show similar ellipsometric data for typical fused silica film taken from Palik’s handbook [127]; (b) Spectral dependence of the refractive index of SiO$_{2+δ}$ films (line E). For comparison, we present n (λ) for several industrially important glasses, including fused silica film [127] (line F), 7059 glass (line C), BK7 from Schott [128] (line D) and crystalline quartz [127] (lines A and B, corresponding to extraordinary (Quartz E) and ordinary (Quartz O) crystal orientation, respectively).

Thus, summarizing this subchapter, we prove the possibility of carbon-free amorphous high-quality Si-based insulator nanoprototyping via the developed single-needle approach. For the first time we present results of all functional physical
properties of purified SiO\textsubscript{2} EBID-grown material, including the combination of compositional, structural, optical and electrical measurements, which suggest utilization of fabricated SiO\textsubscript{2} structures in the fields of nanophotonics, photovoltaics, micro- and nano-electronics, as a high quality transparent insulator.

4.5. Nanofabrication of Ultra-Sharp AFM Tips via EBID from Naphthalene Precursor

In just about any microscopy and imaging technique resolution is the name of the game. In the SPM field quality of each acquired scan is directly related to characteristics of the tip, utilized for imaging, in particular its aspect-ratio and diameter of the tip’s end. Considering that EBID can be successfully used for sharp pillars deposition from Co- [11] and Au-based precursors [36], it was interesting to try out patterning of high-aspect ratio AFM tips from a simpler precursor, such as e.g. naphthalene, and analyze their durability.

For that reason a number of deposition parameters was tested out varying accelerating voltage from 5 to 30 kV and utilizing as low current values as possible. Experimentally the best nanopatterning results were achieved for the C EBID performed in UHR mode at 18 kV, 0.6 nA.

Fabricated tips were quite sharp (Figure 4.33, left), having a diameter of a tip’s end below 30 nm, and the aspect-ratio barely comparable to high-end commercially available AC 240 tips (Figure 4.34), frequently used for AFM analysis.

For the comparative studies 2 µmasch grating samples were selected: TGX01 and TGZ03 represented in Figure 4.35.

In the case of TGX01 AFM analysis, the pyramidal shape hidden for AC240 was demonstrated with a 1.2 µm tall C EBID tip, which diameter at the base was below 100 nm (Figure 4.36, top). Characterization of TGZ03 sample showed that high-aspect ratio e-beam patterned tip can follow 500 nm tall 90° sample’s steps more precisely than AC 240 tip (Figure 4.36, bottom), proving the superiority of EBID fabricated tips. Here even though the ends of the two tips had similar sizes, the difference is observed due to high aspect ratio of our EBID tip and the fact that its diameter does not vary so much with its length.
Later, after a number of AFM scans, quality of the C fabricated tip was checked again with SEM and, as shown in Figure 4.33 (right), its shape is identical to originally patterned (see Figure 4.33, left), proving excellent durability of the EBID tips grown from naphthalene precursor.

**Figure 4.33.** SEM images of ultra-sharp high aspect ratio “Carbon-EBID” AFM tip, with the view at a 52° tilt (*Left*) image of the tip deposited at 18 kV, 0.6 nA; *Right* image of the same tip after acquisition of several AFM images.

**Figure 4.34.** SEM images (with the view at a 52° tilt) of a high-end commercial tip – AC 240 tip, frequently used for AFM analysis. *Right* figure represents a zoomed view of *Left* figure.
Figure 4.35. µmasch grating samples:

(Left) TGX01, with periodic pyramidal structure of 900 nm step height; and

(Right) TGZ03, with periodic 500 nm tall rectangular bars.

Considering the superb performance of the C EBID tips, especially their superior accuracy in tracking tall high aspect ratio structures (similar to many of those we produce via EBID), we used such home designed tips for AFM analysis of most of the samples produced in the course of the work described in this thesis and some of the obtained images are presented here.
Figure 4.36. AFM section analysis of the (Top) TGX01 and (Bottom) TGZ03 µmasch grating samples, both acquired with the commercial AC 240 tip and C EBID tip.
CHAPTER 5: CONCLUSIONS AND PERSPECTIVES

5.1. Conclusions

*Electron-Beam-Induced Deposition is the Future of Advanced Nanoprototyping!*

Electron-Beam-Induced Deposition is a unique nanoprototyping method allowing creation of nano- to micro-scale planar and 3D structures with tailored functional properties, which can be subsequently utilized in a number of nanotechnology areas, such as e.g. electronics, plasmonics and biotechnology, to name just a few. However, besides all benefits this state-of-the-art process has certain drawbacks. One of the major EBID constraints – poor purity of as-deposited materials – was thoroughly investigated in Thesis for a number of gas chemistries.

Significant chemical composition enhancement was achieved for EBID materials grown from Co$_2$(CO)$_8$, Me$_2$Au(acac) and TEOS precursors after exploring the following purification approaches:

- Deposition onto a preheated substrate.
- Post-deposition annealing: in air and in controlled atmosphere.
- Deposition in the presence of reactive gases.

It was established that deposition from Co$_2$(CO)$_8$ precursor at *elevated temperatures* (> 55 °C) leads to growth of pure nanocrystalline Co with transport and magnetic properties close to the values of bulk crystalline cobalt, in particular 22 µΩ cm resistivity and 1.55 T saturation magnetization. Moreover, seeded growth regime was discovered for this gas chemistry within the temperature range of 55 °C – 75 °C ± 5 °C. The advantage of this process was in significant increase of Co deposition rate and physical properties improvement as compared to standard EBID.

*Ex-situ post-deposition annealing* of structures grown from Me$_2$Au(acac) resulted in a dramatic purity improvement, from around 12 at.% up to > 92 at.% of Au, rest being C. Thus, for the creation of planar Au structures it was observed that heat treatment in air at 600 °C during 1 hour is sufficient enough condition, while for patterning of periodic 3D Au structures (e.g. pillar arrays), it was recommended to use lower temperature for annealing (e.g. 400 °C), faster heating rate (e.g. 1.26 °C/s), shorter annealing time (e.g. 30 min) and preferably oxygen atmosphere to facilitate
the best degree of originally patterned shape preservation, distortion of which could occur as a side effect of heat treatment. As well, for more accurate deposits’ shape control during annealing process, it was suggested to take into consideration the height-to-area factor (HAR) and to utilize Ta buffer layer, which stimulated formation of fine-granular densely-packed Au structure after purification step, due to its outstanding wetting properties. A wet etching method for subsequent removal of the buffer layer from not-patterned areas, required in some cases for further applications, was also described.

For patterning of Si-based oxides from TEOS precursor we presented a significantly improved gas-assisted purification strategy, based on intermixing of oxygen and precursor gas molecules in a single needle, thus, allowing for considerably simplified EBID process. We analyzed, for the first time, all functional physical properties of purified SiO$_2$ EBID-grown material, including combination of compositional, structural, optical and electrical measurements. Our results demonstrated that fabricated material is a carbon-free insulator with amorphous structure and optical properties similar to high-quality transparent silica glasses.

### 5.2. Outlook to the Future

Considering that possibility to deposit pure conducting, insulating and magnetic materials, with tailored shapes and properties, has now been shown for EBID technique, the next logical step is to attempt design of components and actual nanodevices via e-beam-assisted deposition.

As well it is valuable to proceed with further development and tailoring of purification strategies for other gas chemistries, to further expand application range.

Among the long-term goals in this area, it is beneficial to aim towards automation of the EBID fabrication process and the subsequent scale-up production of prototyped structures for a variety of modern nanotechnology applications.
5.3. References


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