The Second International Workshop on
Focused Electron Beam Induced Processing
FEBIP 2008

July 6-8, 2008, Thun, Switzerland

ABSTRACT BOOK

Organized by

Ivo Utke
Empa, Swiss Federal Laboratories for Materials Testing and Research

Scientific Committee

Patrik Hoffmann
EPFL, Swiss Federal Institute of Technology
Ivo Utke
Empa, Swiss Federal Laboratories for Materials Testing and Research
Dear FEBIP friend,

Two years is the right time span to meet again with your peers to share novel results and to introduce colleagues from adjacent fields to a promising but highly specialist technologically demanding research field; especially when it covers a large variety of interdisciplinary and complementary domains of fundamental science and technology.

An exciting example is local gas-assisted Focused Electron Beam Induced Processing (FEBIP). Here the domains range from solid state physics to physical chemistry to synthetic chemistry; from fluid dynamics to mechanical engineering, from surface analysis to optics, electronics and life sciences – all framed by the buzz word nanotechnology.

Industrial applications already exist, many exciting demonstrators for novel applications have been produced by FEBIP and there is still room for growth. Many questions are open – many surprising new results have been observed – our challenges for the future.

The 2nd FEBIP workshop in the wonderful relaxing atmosphere at Lake Thun aims to update the community with the recent news in FEBIP: impressive results concerning deposit purity, deeper understanding of the FEBIP mechanisms, smart technical solutions for FEBIP experiments; and also tries to open doors to novel technologies on one side and innovative approaches for new precursors and deposits on the other side. Uses for FEBIP will grow in future and this anticipated growth is reflected by the number of contributions to this workshop dealing with applications.

The main aim of the workshop is bringing together the world’s specialists in gas-assisted focused electron and ion beam induced processing in a fertile environment, offering sufficient time for discussions and seeding presentations of specific topics. Our FEBIP community is growing: the 85 participants registered at the time when this book will go to print will present 50 contributions either as oral presentations or as posters in the scientific program. Let us spur our efforts to increase the impact of FEBIP into the 21st century technology platform, and with the good will and motivation of all of us, make this workshop a nice, interesting, fruitful, and exciting event.

Welcome to Thun,

Ivo UTKE and Patrik HOFFMANN
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# Scientific Program - Talks

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<td>O1 Keynote Lecture</td>
<td><strong>Ultimate Resolution in EBID: Modelling, Problems, and Perspectives.</strong></td>
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<td><strong>Overview of FEBIP Simulation, Experimentation and Recent Applications.</strong></td>
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<td>Klaus Edinger et al., Carl Zeiss SMS, Germany</td>
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<td>O4 Keynote Lecture</td>
<td><strong>The role of growth kinetics in high resolution electron beam induced etching and deposition.</strong></td>
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<td><strong>Electron Induced Chemistry; Chemical Control at the Molecular Level.</strong></td>
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<td><strong>Electron Driven Processes in Ices: Surface Functionalization and Synthesis Reactions</strong></td>
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A) Gas Injection Systems

P1: A Modular Ultra-High Vacuum Compatible Gas Injection System with an Adjustable Gas Flow
D. Klingenberger and M. Huth.
Physikalisches Institut, Goethe-University, Frankfurt am Main, Germany, klingenberger@physik.uni-frankfurt.de

P2: Multiple-Gas-Injector for Electron Beam Induced Deposition
H.D. Wanzenboeck1*, G. Hochleitner1, A. Rosenthal2 and W. Buehler2
1 Vienna University of Technology, Institute for Solid State Electronics, A-1040 Vienna, Austria, Heinz.Wanzenboeck@tuwien.ac.at
2 Carl Zeiss NTS, D-73447 Oberkochen, Germany, W.Buehler@smt.zeiss.com

P3: Optimization of Nozzle-Based Gas Injection Systems for Focused Electron- and Ion-Beam Induced Processing
V. Friedli, J. Michler and I. Utke
Laboratory for Mechanics of Materials and Nanostructures, Swiss Federal Laboratories for Materials Testing and Research (EMPA), 3602 Thun, Switzerland, vinzenz.friedli@empa.ch

P4: Progressing in FEBIP in a JEOL 6300F
L. Ajili, B. Afra and P. Hoffmann
Advanced Photonics Laboratory, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland, patrik.hoffmann@epfl.ch

B) Electron Impact Molecule Cross Sections

P5: Focused Electron-Beam-Induced Deposition of Platinum at Very Low Landing Energies
A. Botman1*, D. A. M. de Winter2 and J. J. M. Mulders3
1 Philips Research Laboratories, High Tech Campus 34, 5656 AE Eindhoven, The Netherlands. Present address: Faculty of Applied Sciences, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands, a.p.j.m.botman@tudelft.nl
2 Utrecht University, H.R. Kruyt building, Padualaan 8, 3584 CH Utrecht, The Netherlands
3 FEI Electron Optics, Achterseweg Noord 5, 5600 KA Eindhoven, The Netherlands

P6: Electron Molecule Collisions and Plasma Modelling Using Quantemol-N and Quantemol-P
N. Doss*, J. J. Munro, J. Tennyson and H. N. Varambha
Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK, natasha@theory.phys.ucl.ac.uk

P7: A Study of the Surface Chemistry and Cross Sections for Electron Induced Dissociation for (CH₃)₃-Pt-C₅H₄CH₃ Using Temperature Programmed Desorption
W.F. van Dorp1,2*, S. Zalkind1, B. Yakshinskiy1, T.E. Madey1, C.W. Hagen2
1 Laboratory for Surface Modification, Rutgers, the State University of New Jersey, 136 Frelinghuysen Road, 08854 Piscataway, NJ, USA, w.f.vandorp@tudelft.nl
2 Charged Particle Optics Group, Faculty of Applied Sciences, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, Netherlands

P8: Overlapping Corrections in Computation of Electron Impact Various Total Cross Sections for BFₓ (x= 1-3) and BClₓ (x= 1-3)
Minaxi Vinodkumar1*, Kiriti M. Korot1 and Chetan Limbachiya2
1 V. P. & R. P. T. P. Science College, Vallabh Vidyanagar – 388 120, Gujarat, India, minaxivinod@yahoo.co.in
2 P. S. Science College, Kadi- 382 715, Gujarat, India
P9: Computation of Electron Impact Total Elastic, Total Ionization and Total Cross Sections for NF_x (x= 1-3)
Minaxi Vinodkumar, Chetan Limbachiya and Kirti M. Korot
1 V. P. & R. P. T. P. Science College, Vallabh Vidyanagar – 388 120, Gujarat, India, minaxivinod@yahoo.co.in
2P. S. Science College, Kadi- 382 715, Gujarat, India

C) FEBID for Nanooptics

P10: High Precision Gold and Platinum Nanostructures Produced via Focused Electron Beam for Usage in Enhanced Raman Techniques
K. Ehrhold1, M. Becker2,1, T. Stelzner, A. Berger2,1, D. Lerose2,1*, S. Christiansen2,1* and U. Gösele1
1Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany
2Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany, sechrist@mpi-halle.de

P11: Fabrication of Plasmonic Gold Nanostructures by Focused Electron Beam Induced Deposition
S. Graells1,2, R. Alcubilla1,3, G. Badenes1 and R. Quidant1,4
1 ICFO - Institut de Ciències Fotòniques, Parc Mediterrani de la Tecnologia, 08860 Castelldefels (Barcelona), Spain. Romain.quidant@icfo.es, simo@salle.url.edu
2Enginyeria La Salle, Universitat Ramon Llull, Quatre Camins 2, 08022 Barcelona, Spain.
3UPC - Universitat Politècnica de Catalunya, c/ Jordi Girona 1-3, 08034 Barcelona, Spain.
4ICREA - Institució Catalana de Recerca i Estudis Avançats, Passeig Sant Joan 10, 08010 Barcelona, Spain.

P12: Focused Electron Beam based Production of Nanostructures for optical spectroscopy
D. Lerose2,1, K. Ehrhold1, M. Becker2,1, T. Stelzner2, A. Berger2,1, S. Christiansen2,1* and U. Gösele1
1Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany
2Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany, sechrist@mpi-halle.de

P13: Fabrication of Titanium Oxide Nanostructures on Au(111) and Si(111) / Si(100) via EBID
Marie-Madeleine Walz, Florian Vollnhals, Michael Schirmer, Thomas Lukaszyk, Hans-Peter Steinrück and Hubertus Marbach*
Lehrstuhl für Physikalische Chemie II, Department Chemie und Pharmazie, and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany, marbach@chemie.uni-erlangen.de

P14: Novel Approach for the Fabrication and Precise Placement of Optical Antennas
Alexander Weber-Bargioni, Bruce Harteneck, Peter J. Schuck and Stefano Cabrini
Molecular Foundry, Lawrence Berkeley National Laboratory, University of California, Berkeley CA USA, SCabrini@lbl.gov

D) FEBIP Lithography on Condensed or Liquid Precursors

P15: Chemical Lithography: FEBIP with SAMs
Armin Gözlhäuser
Universität Bielefeld, Fakultät für Physik, and Bielefeld Institute for Biophysics and Nanoscience (BINAS), 33615 Bielefeld, Germany, goelzhaeuser@uni-bielefeld.de

P16: Electron Beam Induced Deposition of Platinum-Containing Structures at Cryogenic Temperature
M. Bresin1, J. Li1, B.L. Thiel1, K.A. Dunn1 and M. Toth2
1 College of Nanoscale Science and Engineering, University at Albany – SUNY, 251 Fuller Road, Albany, NY, 12203, USA, mbresin@uamail.albany.edu
2FEI Company, 5350 NE Dawson Creek Drive, Hillsboro, Oregon 97124, USA
D) FEBIP Lithography on Condensed or Liquid Precursors - Continued

P17: Development of a Liquid Precursor and a Deposition Process for Carbon and Chlorine Free Direct Writing of Gold
T. Wich1*, T. Luttermann1, M. Necke2, K. Al-Shamery2, F. Gerlach3 and M. Wickleder3
1 University of Oldenburg, Division for Microrobotics and Control Engineering, D-26111 Oldenburg, Germany, thomas.wich@informatik.uni-oldenburg.de
2 University of Oldenburg, Physical Chemistry, D-26111 Oldenburg
3 University of Oldenburg, Inorganic Chemistry, D-26111 Oldenburg

P18: Analysis of Resist Shrinkage by Electron Beam Irradiation
M. Kotera1,2*, Y. Akiba2 and S. Tsuji2
1 Nanomaterials Microdevices Res. Ctr., Osaka Inst. of Tech., 5-16-1, Omiya, Asahi-ku, Osaka, Japan, kotera@alts.oit.ac.jp

E) Electrical Transport Properties of FEB and FIB induced deposits
P19: Tunnel Percolation and Current Path Switching in a Granular Metal
Ch. Grimm*, D. Klingenberg and M. Huth.
Physikalisches Institut, Goethe University, Frankfurt am Main, Germany, c.grimm@physik.uni-frankfurt.de

P20: Superconductivity of Nanoscale Tungsten Grown by Focused-ion-beam Deposition
Wuxia Li*, J. C. Fenton and P. A. Warburton
London Centre for Nanotechnology, University College London, London, WC1E 7JE, UK, wli@ee.ucl.ac.uk

P21: Transport properties of IBID and EBD Pt nanodeposits
J.M. De Teresa1*, A. Fernández-Pacheco1,2, R. Córdoba2 and M.R. Ibarra1,2
1 ICMA, Institute of Materials Science of Aragon, CSIC-University of Zaragoza, 50009 Zaragoza, Spain, deteresa@unizar.es
2 INIA, Institute of Nanoscience of Aragon, University of Zaragoza, 50009 Zaragoza, Spain

P22: Comparison of Ion- and Electron-Beam-Induced Pt Nanodeposits
R. Córdoba1*, J. M. De Teresa2, A. Fernández-Pacheco1,2, P. Strichovanec1, A. Ibarra1 and M.R. Ibarra1,2
1 INIA, Institute of Nanoscience of Aragon, University of Zaragoza, 50009 Zaragoza, Spain, rocorcas@unizar.es
2 ICMA, Institute of Materials Science of Aragon, CSIC-University of Zaragoza, 50009 Zaragoza, Spain.

F) Mechanical Properties and Applications of FEB induced deposits
P23: Stiffness, Density and Quality of High Aspect Ratio Cu/C Nanostructures Produced by Focused Electron-Beam Induced Deposition
V. Friedli, J. Michler and I. Utke
Laboratory for Mechanics of Materials and Nanostructures, Swiss Federal Laboratories for Materials Testing and Research (EMPA), 3602 Thun, Switzerland, vinzenz.friedli@empa.ch

P24: Applications of Electron-Beam-Induced Deposition: Additive Repair of Nano-Imprint Lithography Masks and Mechanical Fixation of Carbon Nanotubes
A. Botman1*, S. F. Wuister2, M. Ovsyanko2 and J. J. M. Mulders3
1 Philips Research Laboratories, High Tech Campus 34, 5656 AE Eindhoven, The Netherlands. Present address: Faculty of Applied Sciences, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands, a.p.j.m.botman@tudelft.nl
2 Philips Research Laboratories, High Tech Campus 34, 5656 AE Eindhoven, The Netherlands
3 FEI Electron Optics, Achteweg Noord 5, 5600 KA Eindhoven, The Netherlands
G) Integration of FEBIP and SIMS

P25: The Integration of EBIE into a SIMS tool: Towards Quantitative Depth Profiles with High Resolution and a Better Understanding of the Etch Mechanisms
N. Vanhove, P. Lievens and W. Vandervorst
1 IMEC vzw, Kapeldreef 75, B-3001 Leuven, Belgium, Nico.Vanhove@imec.be
2 INSYS, Electrical Engineering Department, K.U.Leuven, Kasteelpark Arenberg 10, B-3001 Leuven, Belgium
3 Laboratorium voor Vaste-Stoffysica en Magnetisme, K.U.Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium

H) FEBIP: Deposition, Etching, Reactive Gases

P26: Electron Stimulated Materials Processing for Nanofabrication and Bio-Inspired Synthesis
J. D. Fowlkes, M. L. Simpson, M. J. Doktycz and P. D. Rack
1 Nanofabrication Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States of America, fo2@ornl.gov
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P27: Fabrication of Sub-Beam Size Nanoholes by Controlled Focused Electron Beam-Induced Etching
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Ultimate Resolution in EBID: Modelling, Problems, and Perspectives

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Introduction
In EBID an electron beam is focused on a substrate surface on to which precursor molecules are adsorbed. The electrons induce the dissociation of the precursor molecules such that a solid deposit remains at the surface. When the deposition remains limited to shallow structures (aspect ratio smaller than ~2) the spatial resolution of the technique is better than 1 nanometer. Growing taller structures the electron scattering in the deposit itself will cause a broadening of the structures. From Monte Carlo simulations of the electron substrate and electron deposit interaction we were able to understand this process. Intrigued by the very high resolution of EBID we started to investigate the limits to the resolution. This was done in the environmental Scanning Transmission Electron Microscope (STEM) of ASU at a beam energy of 200 keV, a 0.3 nm probe and W(CO)6 as a precursor gas. Typical precursor gas pressures during the deposition are 10^-3 Torr, and to reduce contamination from the microscope the substrates are held at an elevated temperature of 100-150 °C. We deposited arrays of nanometer sized dots on thin membranes of SiN, amorphous carbon or graphite [1]. The imaging and monitoring of the growth were performed with the annular dark field (ADF, i.e. the current of electrons scattered by the substrate over very large angles) signal. The smallest deposits we have made so far have an average volume of 0.4 nm³.

Statistical effects
Performing EBID experiments aimed at the ultimate spatial resolution we discovered that statistical effects become apparent, that can no longer be ignored [2]. When depositing regular square arrays of dots on thin membranes we found that dots deposited with the same deposition time had different masses, and were displaced with respect to the intended position (see fig. 1). The distribution of masses could be explained from the Poisson noise in the number of deposited molecules. But the distribution in position has not been understood yet. It may be due to the random deposition within the area where secondary electrons are emitted from the substrate, or it may be due to diffusion of the dissociated precursor fragments. It could also be the result of specific surface sites being more effective in binding the precursor molecule prior to dissociation, or binding the solid precursor fragment after dissociation.

Growth control
We have experimented with using the ADF signal, which is proportional to the deposited mass in the beam, to control the deposition [3]. The idea is to monitor the growth with the ADF signal and stop the deposition when a certain preset mass is deposited. This scheme works well to correct for proximity effects which occur when deposits are grown very close to each other. In order to also use it for controlling the growth of ultra-small deposits we tried to detect the stepwise growth of a deposit which would ideally occur when single dissociation events could be registered. This has not been achieved yet, but a fundamental limitation has not been reached yet. We did see steps in the growth curves (see fig. 2) but they corresponded to larger deposited volumes, of the order of 1-2 nm³. It is not clear yet what this means.

Problems and perspectives
When fabricating such small deposits surface physics starts playing a prominent role. There are issues like surface diffusion, generation of surface plasmons, surface charging effects on insulators and migration under influence of electrostatic fields. And the growth rate and purity of the deposits is largely determined by the cross section for dissociation of adsorbed precursor molecules. These cross sections, however, are hardly known for typical EBID precursors. So what is the perspective to solve these problems? Well, the statistical effects are important only for the very small deposits (smaller than approx. 2 nm) and may be dealt with by controlling the growth with the ADF signal. Larger structures, between 2 and 10 nm, can be grown in a well controlled way already (see fig. 3). To address the growth speed and purity issues more knowledge has to be acquired on the dissociation mechanisms. Fortunately, the surface science community is well equipped to measure dissociation cross sections and determine what the
relevant dissociation pathways are. This will aid in designing dedicated precursors that result in cleaner deposits, or in devising mitigation schemes to achieve pure deposits. One good deposition process on one particular substrate material would give EBID an enormous boost as a high resolution lithography technique. The recent interest of surface physicists and chemists in EBID as an application field for their fundamental knowledge is a very promising sign.

References


Fig. 1: Through-dose series of 1 nm dots, both showing the resolution capabilities of EBID and the intrinsic limitation by the fluctuations in number of deposited molecules.

Fig. 2: Volume growth versus time for deposition at 3 different sites on a C foil. The volume axis is calibrated using Atomic Force Microscope measurements of the deposits. The right hand axis represents the average number of dissociation events $\lambda$. The black solid lines are moving averages and serve merely as guides to the eye.

Fig. 3: 4.5 nm diameter W dots on a C foil at 11 nm half pitch, illustrating sub-10 nm deposition control.
Overview of FEBIP Simulation, Experimentation and Recent Applications

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Abstract

The rapid and precise direct-write growth of nanoscale features by electron-beam-induced processing (EBIP) requires the optimization of the growth parameters to maintain nanoscale feature dimensions. The tremendous and complex EBIP parameter space includes the precursor gas pressure, the primary electron beam energy, the electron beam current, surface diffusion rates of adsorbed precursor species, thermal effects on desorption, and the cascade of electron species produced by elastic and inelastic scattering processes. These variables affect the probability of precursor dissociation and hence determine the feature growth velocity and the size of the structure through a series of complex, coupled nonlinear interactions. In the first part of this presentation, a variety of experimental studies will be presented to demonstrate the various electron-gas, gas-solid, and electron-solid interactions that are germane to the electron beam induced processing technique. A dynamic computer simulation based on Monte-Carlo electron cascades in the solid will then be described and compared to various experimental observations [1-3]. A Langmuir adsorption isotherm is assumed for the precursor adsorption and a random walk algorithm is employed to handle surface diffusion.

The second part of the presentation will overview some of the recent experimental EBIP work that our group has done. Specifically we will overview our recent success in growing single crystal nanowires grown from a WF6 precursor [4]. A systematic study correlating various beam parameters and growth orientations to the nanowire microstructure will be described. Additionally we will overview some of our electron beam induced etching studies which includes etching a variety of materials from extreme ultraviolet masking materials [5] and silicon dioxide to carbon nanotubes.

Finally, we will review several applications where we are implementing nanoscale elements fabricated via electron beam induced processing. Recent applications include: nanolithography [6], scanning probe tip editing [7], cellular probes and cellular membrane mimics.

References


Figure 1. Collage of images representing some of our recent EBIP research. Top: SEM micrographs of a series of electron beam induced deposited lines over a high-aspect ratio gap with a representative Monte Carlo EBID simulation. Middle: electron micrograph and selected area diffraction of a single crystal nanowire grown via EBID. Bottom left: SEM image of a scanning probe tip modified via EBIP. Bottom right: SEM images of an array and a high resolution image of ~13.5nm silicon nanowires patterned via an EBID lithography approach. Note the top EBID W layer, the thin photoresist (PR) layer and the reactive ion etched silicon nanowire.
Focused Electron Beam Induced Processing: Modelling, Applications and Research Opportunities


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Although a large number of experimental data on electron beam induced deposition (EBID) and, to a lesser extend, on etching is reported in the literature, many aspects of the involved physical and chemical mechanisms are still poorly understood. However, the kinetics of this complex process can be modelled as a function of (known) instrumental settings such as electron flux, precursor flux and beam steering parameters (e.g. dwell and refresh time) and fundamental parameters such as reaction cross section, residence time and diffusion coefficient. By fitting these parameters to growth or etch rate data obtained under various experimental settings one can gain valuable insight into the validity of the underlying model and the involved mechanism as well as optimize the process in terms of throughput and material composition.

In addition to presenting experimental data on modelling of beam induced chemistry, this paper will illustrate the potential of the technique showing two recent applications in the area of semiconductor fabrication.

With the ever shrinking feature sizes of photo masks, repair and repair validation of current technology type masks has become a substantial cost factor in overall mask production cost. In this context, the introduction of high-resolution electron-beam assisted deposition and etching has been an enabling technology to keep up with the increasing demands on current and next generation photomask repair. We will present an overview of key features of our e-beam based mask repair tool, discuss 45 nm and future node requirement and demonstrate current repair performance for standard binary (Chrome on Quartz) and phase shifting masks. In addition, feasibility studies for the repair of next generation technologies such as EUV mask, EUV blank and imprint template repair will be presented.

In the area of circuit editing focused ion beam tools have been widely used for debugging and rewiring of prototype integrated circuit during the design phase. Again, due to the shrinking dimensions of modern integrated circuits, FIB based processing is reaching its limits in terms of resolution and achievable aspect ratios. We have investigated the feasibility of e-beam based circuit editing and results including high aspect ratio via etching, copper line cutting and backfilling of vias with low resistivity conducting material will be presented.
Fig 1: Pre-repair image of a ~50 nm sized extension defect on a contact hole area of an attenuated phase shift mask (left side). Same area after repair by electron beam induced etching of excessive Molybdenum silicide adsorber material (right side).

Fig. 2: Cross-section of a circuit editing type process step, including etching a via through inter-layer dielectric to the M1 interconnect layer by electron beam induced etching and backfilling the via with conducting material by electron beam induced deposition. Minimum via width is less than 100 nm, with an aspect ratio of 10:1.
The role of growth kinetics in high resolution electron beam induced etching and deposition

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Spatial resolution of electron beam induced deposition (EBID) and etch (EBIE) processes is governed by both the electron flux distribution, and variations in adsorbate concentration at the substrate surface. The concentration profile is determined by a competition between precursor arrival from vacuum and diffusion along the surface, and adsorbate depletion caused by electrons crossing the substrate-vacuum interface. Concentration variations around the electron beam give rise to anisotropic etching or deposition that limits the minimum diameters [1] (Fig. 1), maximum aspect ratios (Fig. 1) and homogeneity (Fig. 2, Fig. 3) of features fabricated by EBID and EBIE. However, the often detrimental effects of adsorbate depletion can be exploited using simultaneous etch and deposition processes which can be used to fabricate unique, high resolution nanostructures [2, 3].

Growth kinetics caused by adsorbate depletion can be simulated using continuum models such as the delocalized models described by Christy (1960)[4] and Toth et al. (2007)[2], and the spatially resolved, radially symmetric model of electron beam induced deposition and etching (EBIED) described by Lobo et al. (2008)[3]:

$$\frac{\partial N_e(r,t)}{\partial t} = s_e F_e[1 - (A_e N_e(r,t) + A_d N_d(r,t))] - \frac{N_e(r,t)}{\tau_e} - \sigma_e f(r) N_e(r,t) D_e \left[ \frac{\partial^2 N_e(r,t)}{\partial r^2} + \frac{1}{r} \frac{\partial N_e(r,t)}{\partial r} \right]$$

(1)

$$\frac{\partial N_d(r,t)}{\partial t} = s_d F_d[1 - (A_e N_e(r,t) + A_d N_d(r,t))] - \frac{N_d(r,t)}{\tau_d} - \sigma_d f(r) N_d(r,t) - \left[ \sigma_e f(r) N_e(r,t) \right] \sigma_d N_d(r,t) + D_d \left[ \frac{\partial^2 N_d(r,t)}{\partial r^2} + \frac{1}{r} \frac{\partial N_d(r,t)}{\partial r} \right]$$

(2)

$$\frac{\partial N_d(r,t)}{\partial t} = - \sigma_d f(r) N_d(r,t) \left[ 1 - \sigma_d N_d(r,t) \right] \sigma_d N_d(r,t)$$

(3)

In equations 1-3, t is time, r is the radial distance from the electron beam axis, $N_e(r,t)$, $N_d(r,t)$ and $N_d(r,t)$ are the number densities of etch and deposition precursor adsorbates and deposited molecules, respectively, and $f(r)$ is the electron flux. The first term in equations 1 and 2 accounts for adsorption of the etch and deposition precursor molecules, where $s_e$ and $s_d$ are their sticking coefficients, $F_e$ and $F_d$ are the molecular fluxes arriving from vacuum, and $A_e$ and $A_d$ are the adsorbate areas. The second term of equations 1 and 2 accounts for desorption and the final term accounts for surface diffusion of the adsorbates, with $\tau_e$ and $\tau_d$ being the etch and deposition precursor desorption times, and $D_e$ and $D_d$ being their respective surface diffusion coefficients. The remaining terms describe electron-adsorbate interactions that give rise to EBIED; $\sigma_e$ and $\sigma_d$ are electron dissociation cross-sections of etch and deposition precursor adsorbates, and $\sigma_{ed}$ and $\sigma_{dd}$ are cross sections for reactions that lead to the volatilization of deposition adsorbates and deposited molecules, respectively.

Equations 1-3 have been used to investigate simultaneous EBIED processes for the fabrication of high resolution, radially symmetric nanostructures. Fig. 4 shows three relative growth rate distributions for structures fabricated using a 4 nm (full width at half maximum) stationary electron beam and currents of 0.4, 0.5 and 0.6 nA [3]. The results illustrate current-mediated control over the deposit growth rate and the inner diameter of the ring-shaped nanostructures.

We will discuss how models such as the above can be modified to account for different types of adsorption behaviour (e.g., that governed by Langmuir and Tempkin isotherms), impurity incorporation in materials fabricated by EBID, and the effects of changes in surface area during deposit growth on the adsorbate concentration and electron flux profile. We will also discuss experimental studies of growth kinetics in which beams with Gaussian and top-hat electron flux profiles were used to manipulate growth kinetics. For example, Fig. 5 shows four deposits grown as a function of the diameter of a top-hat electron beam, and two deposits grown using a highly focused Gaussian beam. Measurements of the vertical and volume growth rates of such deposits made as a function of EBID operating parameters have been used to determine the significance of individual mechanisms behind EBID growth kinetics.
Process spatial resolution can also be improved using consecutive (rather than simultaneous) EBID and EBIE processes such as the one illustrated in Fig. 2, showing the formation of a sub-10 nm gap in a carbonaceous nanowire pre-fabricated by EBID [5]. The ultimate resolution of such EBIE-based processes is often limited by the surface roughening effect seen in Fig. 2 and Fig. 3. This roughening has been ascribed to electron induced modification of the EBID fabricated material. It is believed to be driven by processes such as H–C bond cracking, high order (C=C and C≡C) carbon-carbon bond formation, and H desorption from the film [5], and is exacerbated by anisotropic electron emission from rough surfaces.

References

Fig. 1: Pillars grown using WF₆ precursor, and a focused stationary electron beam with a Gaussian electron flux profile. The pillar aspect ratios were controlled by the beam current and precursor pressure: (a) 39 pA and 133 mTorr; (b) 1.13 nA and 275 mTorr.

Fig. 2: Four frames from an H₂O-assisted EBIE process used to produce a gap in an EBID-fabricated carbonaceous nanowire [5].

Fig. 3: (a-b) Two frames from an EBIE process of a carbonaceous film and a nanowire. (c-d) Digitally enlarged detail from images (a) and (b) showing nanostructure evolution during EBIE [5].

Fig. 4: Nanostructure growth rate distributions predicted by a model of simultaneous etching and deposition [3].

Fig. 5: Deposits fabricated using WF₆ precursor, and electron beams with Gaussian and top-hat electron flux profiles.
Single Step Fabrication of Nanopores

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1. INTRODUCTION

Nanopores have important applications in many fields of nano-science. The fabrication of small pores is still very challenging. For simple pore fabrication, focused ion beam (FIB) milling is commonly used. However, the achievable pore diameter is limited by the beam size and shape and by re-deposition. Recently, solid state nanopore fabrication in Si₃N₄ or SiO₂ has greatly evolved after two methods had been reported by Li et al.¹ and Storm et al.² They found that pre-existing large pores can expand or shrink upon exposure with either low energy ions¹ or high energy electrons². This effect is the result of a competition between ion-induced sputtering or electron-induced erosion and atom diffusion driven by surface tension. A combination of FIB milling and thin film deposition have been also explored to control the pore size.³,⁴ However, it is still very desirable to develop simpler and faster methods for nanopore fabrication. In this work, we report a single step fabrication method of nano-pores by Ion Beam Induced Deposition (IBID). Pore formation is accomplished by exploiting the competition between sputtering and deposition in IBID. The pore size can be controlled by adjusting the ion beam and gas exposure conditions.

2. EXPERIMENTS AND DISCUSSIONS

Our experiments were performed in a dual beam scanning electron microscope (SEM) and FIB system. (CH₃)₃Pt(CpCH₃) and TEOS were employed as precursor gases for Pt and SiO₂ deposition. The pores were fabricated in a 45nm thick Si₃N₄ membrane by 30kev Ga⁺ FIB at normal incidence. The FIB beam size was about 12 nm. After fabrication, samples were immediately transferred to a high-resolution transmission electron microscope (TEM) for imaging.

We have studied the formation of the pores as functions of the Ga⁺ FIB current, dwell time and exposure time. In all cases, arrays of 16 pores have been made. Only dots formed at a low current of 1 pA, while pores formed in the center of the dots at beam currents of 8 pA and 13 pA. This happens because sputtering dominates over deposition in the central area, and deposition dominates in its rim. For constant exposure time, the pore size is smaller at shorter dwell times (see Fig. 1). But no pores formed at the shortest dwell times. Apparently, for the longer dwell times the gas supply is insufficient and milling dominates in a larger area. For a constant dwell time, first the membrane opened rapidly (≤ 0.5 s for Pt, ≤ 1.0 s for SiO₂). With increasing exposure time, the pore closed again (see Fig. 2). The closing occurs because a large portion of the ions passes through the pore and the beam does not remove as much material as before. Still, deposition at the sidewall of the pores is caused by the primary ions and secondary atoms and electrons. It does not decrease as much as sputtering and finally it dominates over sputtering. The composition of two Pt pores were measured by STEM line scans and X-ray spectrometry (see Fig. 3). The signals of Pt and Si overlap for both small and large pores. It indicates that the in-diffusion of Si happens during IBID. Whether this in-diffusion is driven by platinum silicide formation has to be further investigated.

3. SUMMARY

We have demonstrated a new efficient method to fabricate nano-pores by IBID through controlling the balance between sputtering and deposition. Arrays of sub-10nm pores have been fabricated in a single step. The pore diameter can be controlled by adjusting the usual FIB and IBID parameters. It overcomes the main limitation of FIB milling. There is no need of preceding and succeeding treatments, and no high requirement of membrane thickness. Apart from simplicity and speed, this method offers the additional advantage of a broad choice of membrane and deposition materials.

References
Figure 1. (a) The dependence of pore diameter on dwell time of 8 pA 30kev Ga\(^+\) for Pt deposition (exposure time 4 s per pore) and 13 pA for SiO\(_2\) deposition (exposure time 2 s per pore). TEM top views (bright field) of pores formed with Pt IBID (b) 0.1 ms dwell time (only a Pt dot formed); (c) 2 ms dwell time; (d) with SiO\(_2\) IBID 5.0 ms dwell time.

Figure 2. (a) The dependence of pore diameter on exposure time for 30kev Ga\(^+\) for Pt IBID (dwell time 0.5 ms) and for SiO\(_2\) IBID (dwell time 1.0 ms); TEM images (bright field) of pores formed with Pt IBID (b) 0.5 s exposure time per pore; (c) 11 s exposure time; (d) with SiO\(_2\) IBID 1 s exposure time; (e) 15 s exposure time.

Figure 3. STEM X-ray spectrometry line scans for Pt and Si. Same dwell time (0.5 ms) but different exposure times: 0.25 s or 4 s per pore; pore diameters are 22 nm and 41 nm, respectively.
Electron-driven chemistry and physics of isolated molecules

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The invention of Focused Electron Beam Induced Processing (FEBIP) [1, 2] opens an extremely interesting application of electron-driven chemistry and physics. As such it is of great interest to the traditional community studying electron-molecule collisions. The challenges are to provide suitable cross sections which would, on the one hand, contribute elucidating the FEBIP mechanisms, and on the other hand, and in an ideal case, provide inspiration for improving FEBIP performance.

Early electron-molecule cross section measurements started already in the 30’s, but the field has become very active in the 70’s after the discovery of resonances (transient negative ions, which can increase the cross sections by several orders of magnitude). The subsequent era of ‘chase for resonances’ brought a deep understanding of the mechanisms of electron collision processes. These early days were reviewed by Schulz [3]. A problem with most of the early data is that the absolute magnitudes of the cross sections were not measured.

There were two major application areas which, apart from basic scientific interest, motivated and influenced the electron-molecule collisions studies. One was (and still is) the desire to provide basic data for the modeling of low-pressure plasmas [4,5], widely used for integrated circuit production and other areas of technology. Electron energy distribution function (EEDF) in plasmas generally peaks at 2-5 eV. Ionization and electronic excitation processes are thus reached only by a small minority of the electrons, the high energy tail of EEDF. At the same time, all ionization and electronic excitation processes occur close to threshold. Measurements aiming at plasma understanding thus concentrated at energies up to 20 eV and threshold phenomena were important. Another specificity of these measurements was that all cross sections are important in the plasmas, in particular including the elastic and vibrational excitation (VE), which do not directly contribute to chemical change but contribute to determining the EEDF. A great effort consequently went into measuring and calculating the elastic and VE cross sections.

A more recent area of application is concerned with the damage to living tissue caused by ionizing radiation. Here also, a cascade of ionizing events results in a “shower” of secondary electrons, the majority having low energies. A period of great activity in this area was initiated by the discovery of Sanche and coworkers, that these majority slow electrons cause a dramatic damage to DNA despite their low energies [6,7].

Measurements motivated by the above two applications thus concentrated at energies up to 20 eV. Elastic and VE cross sections were often measured and calculated. The plasma-relevant and scientifically intriguing threshold phenomena were studied [8].

The specific needs of FEBIP place emphasis on different aspects of the cross sections. In FEBIP the majority of the “shower” of the secondary electrons is dissipated in the bulk, does not reach the molecules adsorbed on the surface and does not contribute to chemical change of the precursor. As a consequence, the fraction of the useful chemistry due to primary electrons, with energies of many keV, is expected to be larger than in the gas phase plasma and bulk biological applications mentioned above [1, 2]. The knowledge of the cross sections has been shown to be important, however, and to influence the resolution and other parameters of FEBIP [2, 9]. In FEBIP elastic and VE cross sections appear less important and emphasis is on cross sections for chemical change, primarily dissociative electron attachment (DEA), dissociation into neutral fragments, ion pair formation (bipolar dissociation) and (dissociative) ionization.

The measurements of dissociation into neutral fragments has been notoriously neglected because neutral fragments are more difficult to detect than charged fragments. There are only few measurements available, for example by the chemical gettering technique [10], threshold ionization [11,12], and methods using fast neutral beams. Interesting are the recently developed methods to measure absolute cross sections for chemical reactions in cryogenic matrices [13]. Finally, the precursor molecules for plasma applications (typically N2, O2 and small fluorinated molecules like CF4) and for biological applications (typically nucleic bases) differ from those relevant for FEBIP (metal organic compounds) [1, 2].

As a consequence of what has been written above, not many cross sections directly relevant to FEBIP can be found in the literature. Cross section which include neutral dissociation and which cover sufficiently wide energy ranges have been measured for several molecules, mostly of plasma relevance, like CF4 (page 6 of ref. [5]). When the requirements of FEBIP on the cross sections are defined, more suitable measurements can be performed in the future.
An ultimate goal would be the control of the chemical aspects of the deposition. Electron-driven chemistry appears suitable for this aim, since, at least in the dissociative electron attachment (DEA), it is often observed that the course of the chemical process depends on the incident electron energy (state-selective chemistry), or that different substance classes react very differently to electron impact at given energies. DEA to alcohols could serve as an example of the former reaction, where isotope substitution revealed that the hydroxyl group is dissociated with electrons of about 6.5 eV energy, whereas the alkyl group is dissociated by electrons of 8-9 eV energy [14]. As an example of the second situation, hydroxyl compounds undergo DEA at about 6.5 eV, whereas ethers do not [15]. Unfortunately, it appears difficult to make use of this specificity in FEBIP, because the electron energy distributions can not be influenced directly.

More promising appears a suitable choice of precursors, which are either very reactive, or unreactive, to very slow electrons. This will affect the relative importance of secondary electrons even for a given EEDF. Azides could serve as an example of the former class of compounds [16], saturated compounds as an example of the second class [14,15].

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References
Electron Beam Lithography (EBL) has been identified by the international microelectronics industry as a methodology that has great potential for the fabrication of the next generation of micro- and nano-electromechanical devices. EBL uses a highly focused beam of electron to scan across a pre-prepared surface to produce well defined structures of almost any shape. Since electrons have a shorter wavelength than the photons used in traditional photolithography, EBL has the potential to produce structures below 50 nm. Examples of structures made by electron beam irradiation of a self-assembled monolayer are shown in Figure 1.

![Silicon nanostructures made by e-beam lithography with a self-assembled monolayer resist. Left: line pattern with 100 nm period; Right: single Si lines with widths of (a) 30 nm on Si(100), (b,c) 35, 11 nm on Si(110)](image)

Future nanoscale surface patterning processes require not only the spatial patterning shown in figure 1 but also chemically selective modification of the surface such that each surface may be ‘tailored’ for its specific purpose, for example the development of biochips. Current electron beam lithographic technologies typically use electron energies ranging from a few keV to 100 keV. This yields high resolution, stable conditions and thus allows robust industrial production processes. However the chemical specificity of the exposure is generally low. In contrast low energy electrons (electrons with well-defined energies below the ionization threshold of the material to be modified (<10eV)) are capable of both chemical selectivity and surface functionalisation. This is due to the ability of low energy electrons to initiate and effectively drive selective bond cleavage processes in molecular systems and represents one of the most exciting advances of recent molecular science. The chemical selectivity is controlled by the kinetic energy of the electron or by the choice of functional groups of the target molecule.

The collisional process responsible for such site selectivity is that of Dissociative Electron Attachment (DEA): e⁻ + XYZ → XYZ⁻ → X⁻ + YZ where, XYZ⁻ is a transient negative ion (TNI) which decays (almost instantaneously) to produce a negatively charged fragment X⁻ and a neutral counterpart(s). In the condensed phase, or on a surface the neutral (and generally highly reactive radical products) may then react further with neighbouring molecules or with the surface itself causing the local chemical processing YZ + AB → AYZ + B.

Since DEA is a resonant process, it is limited to a narrow incident energy region (typically < 1eV). Therefore, by tuning over a wide energy range, different resonances and hence different decay paths of the TNI can be induced each with specific products. Hence low energy electron controlled lithography provides an ideal methodology for surface patterning but, since Coulomb inter-electron repulsion always becomes more severe for lower electron energies, it is harder to focus such low energy electron beams and hence achieve the high spatial resolution required in surface patterning.
One possible method for overcoming such problems is to adopt Scanning Tunneling Microscopy (STM) as an electron source for lithography. An STM tip operated in so-called field emission mode is an electron source with high local electron current densities (a typical tunnelling current of 1 nA being equivalent to current densities of up to $10^{10}$ A/m²) that are difficult to realize with conventional electron sources. Since the electron energy can also be controlled with meV resolution, electrons from the STM tip can be tuned to the resonance energy of any DEA processes allowing precise bond selectivity. Furthermore the spatial resolution of the irradiating electron source, although depending on the tip’s radius or curvature, can be as low as 2-4 nm. Using an STM tip as a source of low energy electrons therefore may allow unprecedented chemical control on the nanometre or, indeed, subnanometre scale making it the ideal e-beam lithographic technique (Figure 2).

In this review talk I will discuss several examples of how DEA may selectively break chemical bonds in molecular species, including inducing damage in larger biomolecular systems (Figure 3) such as DNA. I will then review how DEA has been as the precursor for inducing chemical reactions in thin films and within condensed molecular ices. For example it has recently been demonstrated that DEA of acetonitrile ($\text{CH}_3\text{CN} + e^-(2\text{eV}) \rightarrow \text{CH}_2\text{CN}^- + \text{H}$) may be used in the functionalization of hydrogenated diamond to attach organic groups to surfaces the released H reacting with surface hydrogen to create a dangling bond to which the larger fragment attaches under electron detachment. The applications of such processes in a variety of fields from Astrochemistry to Radiation Chemistry and cancer therapy will be discussed. I will then review the state of the art of Scanning Tunnelling Microscopy as a chemical tool before discussing the opportunities for developing such techniques for more commercial electron beam lithography. Opportunities for collaboration between researchers exploring electron induced Chemistry, STM and surface processing will also be discussed with the aim of developing novel research topics.

**References**

Electron Driven Processes in Ices: Surface Functionalization and Synthesis Reactions

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The ability to control and drive chemical reactivity in the condense phase is a major challenge of modern research. Upon interaction with condensed molecules electrons drive bond cleavage thus generating a population of very reactive species in the condensed medium. These species may interact either within the volume to synthesize new molecules or with the substrate surface and be bound to this substrate. The former reaction is known as electron induced synthesis [1] and the latter one as electron induced surface functionalization [2]. In the case of high-energy electrons the chemical specificity is low due to the large number of dissociative open channels. In contrast electrons with energies below ionization threshold of the exposed matter are capable of selective bond cleavage associated with Dissociative Electron Attachment (DEA) mechanism.

Electron interaction with condensed molecules on hydrogenated diamond substrate will be discussed [3]. In particular electron induced functionalization of diamond surfaces by CH\textsubscript{2}CN groups (see Fig. 1), decarbonylation reactions in condensed films of pure organic acids RCOOH (R = H, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}, CF\textsubscript{3}), and carbamic acid formation in CO\textsubscript{2}:NH\textsubscript{3}, HCOOH:NH\textsubscript{3} and CF\textsubscript{3}COOH:NH\textsubscript{3} binary ice mixtures will be presented.

References


\begin{equation}
\text{CH}_3\text{CN}+e^{-}(\sim 2\text{eV}) \rightleftharpoons (\text{CH}_3\text{CN})^{-} \rightarrow \text{H}^+ + \text{CH}_2\text{CN}^- \quad \text{(1)}
\end{equation}

Fig. 1: Proposed mechanism for diamond functionalization by electron irradiation at 2 eV of condensed acetonitrile CH\textsubscript{3}CN. Step 1: DEA process leading to the formation of hydrogen radicals and anions [CH\textsubscript{2}CN\textsuperscript{-}]. Step 2: Depassivation of the hydrogenated diamond surface via recombinative abstraction of H atoms by H\textsuperscript{+} radicals leading to the release of molecular hydrogen and the creation of an active site on the substrate. Step 3: Simultaneous bonding of H\textsubscript{2}CCN chains by their C or N terminal atoms on vacant dangling bonds of diamond and electron ejection in vacuum or flowing through the substrate. From [3].

Acknowledgements

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**FEBIP Applications in Semiconductors**
*From Conceptual Research to Manufacturing*

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**General review**

The use of focused beams of photons, ions and electrons to induce physical and chemical changes has long been researched for a broad range of materials and wide variety of applications. Much research has been devoted by the academic community to fundamental understanding of beam induced processes of deposition, etching and material alteration. The knowledge gained from such basic research enabled the development of beam induced processes into industrial applications from prototyping to manufacturing, such as recording head alteration, integrated circuit (IC) probing, electrical contact to nanowires, miniaturization of field emitters, fabrication of photonic crystal arrays, photolithographic mask repair and IC device editing and debug. Circuit editing and mask repair are two niche, but indispensable, applications of focused ion and election beam induced processes in production in the semiconductor industry. With the continuation of Moore’s law in driving the advancement of semiconductor technology and manufacturing, their applicability in these fields for nano-structuring applications will require continuous process improvement as well as new beam-induced chemistries to meet the stringent requirements for defect control and materials compatibility.

Intel performed its first mask repair using focus ion beam (FIB) technology in 1985 on the 3\(\mu\)m process technology node. Three years later, the first internal circuit edit (CE) was performed on the 80486™ microprocessor to enable it to boot Microsoft Windows™ on first silicon. In 2003, Intel installed the industry’s first electron-beam mask repair tool, and an alternating phase shift mask was successfully repaired for 65nm Si production in 2005. These milestones marked the approximate beginning of the era of using beam induced direct processing to rewire and modify semiconductor devices and masks for semiconductor production.

This invited lecture provides an overview of focused electron beam-induced process (FEBIP) for advanced mask repair from conceptual research to production at Intel. It highlights some key milestones in realizing this technology, including an assessment of the extendability of various technologies, definition of production-worthy requirements, and importance of synergy in process development and equipment commercialization. Descriptions will be given using examples representing binary Cr-on-glass, phase-shifting and extreme ultraviolet (EUV) lithography masks, including repair qualification. Figures 1 shows a repair example.

Photomask repair is a process of editing local pattern structures by adding or removing materials in order to restore a defective mask to good lithographic condition and, in many instances, it is an enabling step for yielding a defect-free mask. Mask shops have put ever increasing emphasis and effort in mask repair at the back end of the production line to fix every defect possible in order to restore an otherwise defective mask. It has become ever more challenging to repair advanced photomasks to meet the critical defect specifications and tight pattern requirements. Specifically, the use of aggressive optical proximity correction structures, resolution enhancement techniques, such as phase-shifting, and entirely new mask types, such as the reflective Mo-Si multilayer (ML) masks employed for EUV lithography places the need for stringent lateral and vertical dimensional control within a few nanometers. A capable repair process removes the defect with sufficient placement precision while at the same time preserves the optical integrity of the repaired site. This essentially requires also a damage-free process. The majority of the defects require a removal process with high selectivity beam-induced chemical etching. Proper selection of etch gases and beam scan control are key process parameters. Due to the randomn nature of the defects, the repair process is the most manual operation in mask production. Therefore, process control is critical. FEBIP has been demonstrated the capability for meeting these challenges. Areas of process development will be discussed in FEBIP for mask repair applications in support of the aggressive lithography roadmap.

**FEBIP for ML and soft defects reduction on EUV mask**

This part of the presentation will discuss the potential of FEBIP in emerging applications beyond pattern defect repair, in hope of sparking interests in further applied research. Particularly, high
spatial resolution, damage-free and flexible beam chemistries are attractive advantages for addressing one of the top risks in EUV lithography – mask defects. These may include the suppression of phase defects in a reflective Mo-Si multilayer stack and the localized removal of contamination and soft defects from a EUV mask. We have investigated the feasibility of rendering a ML phase defect to reduce its printability on wafer, by means of localized silicidation of Mo-Si interfacial layers. The concept is depicted by a schematic in Figure 2. The remaining challenge is to develop a focused electron beam of high current density at short pulses and constrain the beam energy to a small volume near the surface to achieve efficient silicide formation. The combination of a sensitive ML surface (damaged by wet cleaning chemistries) and no pellicle protection (requiring frequent cleaning) presents a set of unique challenges for EUV mask cleaning. Soft defects most often contain carbonaceous and oxide materials, which are believed to be suitable for removal by FEBIP. Figure 3 shows an example of organic contamination on a mask. The use of FEBIP can potentially be complimentary to traditional global wet cleans (i.e., cleaning the whole mask surface). This brings two positive effects – reducing the number of global cleaning cycles and eliminating the need for aggressive, damaging wet cleaning chemistries. Such processes using beam-induced chemistries can also be integrated into other tool set for in-situ soft defect cleaning.

Fig. 1: Example of FEBIP repair for a phase shift mask.

Fig. 2: Schematic depiction of the suppression of a Mo-Si multilayer phase bump through interfacial silicide formation by localized heating such as e-beam.

Fig. 3: A Typical organic contamination (15nm thick in this example) on a EUV mask surface between two absorber lines.

References


Creating Pure Platinum Nano-Structures by Focused Electron-Beam-Induced Deposition: Challenges and Successes

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Electron-beam-induced deposition [1] (EBID) allows the rapid fabrication of three-dimensional nano-devices and metallic wiring of nano-structures within a scanning electron microscope (SEM). The deposited material depends on the precursor chosen; the decomposition of the gaseous precursor is caused by the interaction of an electron beam with a solid substrate. Typical applications of EBID include contacting carbon nano-tubes [2], and growth of tips for field emission [3] and for magnetic force microscopy [4].

Deposited structures often contain undesirable contaminants such as carbon or oxygen as a result of species present in the precursor or from deposition conditions. Previously [5] we have demonstrated that, after deposition of platinum structures from methylcyclopentadienyl-platinum-trimethyl (MeCpPtMe3) in a scanning electron microscope (SEM) with a focused electron beam, an oxygen ex-situ post-treatment at elevated temperature (above 300 °C) is able to remove a large amount of carbon from the deposited structures and hence improve the conductivity (fig. 1) by three orders of magnitude; the platinum content increasing from 15 to 70 at.%. Now we show that a similar ex-situ post-treatment, this time with hydrogen radicals, performed at 150 °C, removes carbon completely from a 30 nm layer at the top of the deposited structure (fig. 2). 30 nm appears to be the penetration depth, or at least depth of interaction, of the hydrogen radicals in the deposited material. Indeed TEM analysis reveals that this layer becomes polycrystalline platinum.

We demonstrate that the as-deposited carbon-rich platinum structures do not have a constant resistivity; with time they undergo an ageing process apparently due to oxidation. Structures stored in air at room temperature suffer a gradual increase in resistivity, going from $2 \times 10^5 \ \mu\Omega\cdot\text{cm}$ to $2 \times 10^8 \ \mu\Omega\cdot\text{cm}$ over 55 days (fig. 3). We describe how this oxidation process can be prevented completely by simply covering the deposited structures with an insulating, electron-beam-induced deposition of tetraethyl orthosilicate (TEOS). The resulting structures have a resistivity of $1.6 \times 10^3 \ \mu\Omega\cdot\text{cm}$ which is the lowest ever recorded for an electron beam induced deposit and this precursor.

To mitigate the inclusion of carbon in deposits, a new carbon-free precursor, tetrakis trifluorophosphine platinum can be used [6]. We have performed thin-structure depositions from this precursor in an SEM with a focused electron beam. Transmission electron microscopy and electron energy loss spectroscopy (EELS) reveals that phosphor clustering occurs (fig. 4). The size and amount of these clusters depend on the thickness of the structure.

References

Figures

**Fig. 1:** SEM image (at 70° tilt) of a typical EBID-deposited structure across four gold electrodes on Si$_3$N$_4$ for four-point-probe resistivity characterization. The halo does not contribute to the measurement in a significant manner.

**Fig. 2:** STEM-HAADF image of part of the treated sample, viewed in cross-section. On the bottom, the silicon nitride substrate. At the top, the TEOS protective layer resulting from the FIB cross-section process. In the middle, a platinum deposited structure. The presence of a 30 nm dense carbon-free layer at the top of the structure (confirmed by EDX) can be observed.

**Fig. 3:** The measured voltage drop across the EBID-deposited structure for 1 nA (hence a measure of resistivity) is shown as a function of time after the structures are exposed to air.

**Fig. 4:** STEM-HAADF images of nine different thin deposits, with increasing thickness (deposition time). The presence of whiter areas (substructure) can be seen whose number and size increase with deposit thickness. Electron energy loss spectroscopy mapping reveals these clusters are predominantly phosphor.
Live SEM imaging of current-driven structural transitions in suspended Pt nanowires grown by EBID

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Results
Electron beam-induced deposition (EBID) performed by lateral shift of the beam from an elevated edge is a powerful method to obtain suspended structures with reduced lateral dimensions, because of the lack of secondary emissions from the substrate, and complex 3D shapes [1]. In a recent work we have performed electrical characterization of suspended nanowires (SNWs) grown from a metallorganic Pt precursor with water vapour assistance, showing a puzzling structural evolution under the electrical measurement [2].

In the present paper, the in-situ characterization by means of a two-probe nanomanipulator system is improved with live SEM video recorded during the I-V measurement, which allows to investigate the Pt nanocrystals dynamics during the transition. TEM analysis of the transformed SNWs is also presented.

SNWs, with dimensions of about 600nm-length and 20nm-diameter, are connecting the tips of Pt pillars grown on opposite Au electrodes, patterned by FIB-lithography on a thin membrane. The gap between the electrodes, below the SNW bridge, is realized by opening a slit into the membrane in order to enable TEM observation of the wires and to avoid on-substrate deposition.

I-V measurements within a range of few hundreds of mV show an ohmic behaviour, with an improvement in conductivity and onset of a structural evolution as subsequent I-V cycles are applied. Typical resistivity after a couple of I-V cycles (-0.1, 0.1 mV range) is around 8-10 x 10^{-5} Ω m, better than values usually reported for on-substrate growths. As the voltage range exceeds 1 V, current departs from the linear trend, rising with a polynomial behaviour, and structural evolution becomes dramatically evident (see Fig. 1). Transition consists of a sudden coalescence of the Pt nanocrystals, which have an original size of 2-3 nm and are homogeneously dispersed into a carbonaceous matrix in the as-deposited structure [3]: Pt grains as large as 20 nm, separated by even wider gaps, are formed within the carbonaceous matrix. When voltage is further increased to 3 – 4 V, migration of the grains from the centre of the SNW to the ends is observed, transforming the central region into a Pt-depleted carbonaceous structure. After this evolution SNWs can carry currents up ~ 50 – 80 μA, corresponding to current densities of the order of 10^7 A/cm², and when they eventually brake they remain stiff. Similar electrical characteristics have been reported for amorphous carbon wires undergoing transition to graphitic phase by the injection and alternated motion of metal nanoparticles [4]. TEM observation of the transformed SNWs (Fig. 2) shows sheet- and ring-like structures into the carbonaceous matrix that are consistent with a graphitization-like process.

References
Fig. 1: Current-Voltage characteristic of a SNW grown from Pt precursor and water vapour. Snapshots taken from the simultaneous SEM video are shown, corresponding to: (a) SNW just before and (b) after Pt-grains coalescence, (c) central region depleted of the Pt-grains migrating to the wire ends and (d) SNW breaking in the middle with a nanosize gap.

Fig. 2: (a) SEM and (b) TEM image of a SNW grown from Pt precursor, after a "high" voltage I-V cycle having induced central region depletion of the Pt-grains (similar to snapshot (c) of Fig. 1). In the TEM image the presence of sheet- and ring-like structures in the carbonaceous material is evident.
Fabrication and analysis of buried iron silicide microstructures using a focused low energy electron beam

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Abstract

In recent years, iron silicide compounds have attracted considerable attention due to their unique properties. In particular, orthorhombic $\beta$-FeSi$_2$ with a direct energy gap of 0.85 eV [1], is an attractive compound because it is applicable for optical device materials. In addition, other iron silicides as well as $\beta$-FeSi$_2$, are interesting materials due to their transport properties [2]. Therefore, these iron silicides are extraordinarily important materials for basic research and also potential device application in silicon-based technology.

In this study, we fabricated iron and iron silicide microstructures on an Si(100) clean surface via electron-beam induced deposition of Fe(CO)$_5$ multilayer and subsequent annealing. The fabricated microstructures were in-situ analyzed by Auger electron spectroscopy (AES) and scanning electron microscopy (SEM).

All the experiments were conducted in a custom-made ultrahigh vacuum system. The base pressure was below 10$^{-10}$ Torr. This system includes an electron gun (Apco mini-EOC), a scintillation counter for SEM, and a double-pass cylindrical mirror analyzer (CMA) (ULVAC-PHI 15-255G) for AES measurements. The electron gun can generate a focused low energy electron beam (0.05-2 keV) via electrostatic lenses, with a minimum spot size of diameter ~25 nm at 2 keV. The details of the system have been described elsewhere [3].

In order to fabricate iron microstructures, electron induced deposition of Fe from Fe(CO)$_5$ was used in this study. The details of the whole process are described in Fig. 1. All experiments for the fabrication of iron structures were performed with $E_p = 2$ keV, $I = 0.2$ nA, where the spot size of the electron beam on the sample surface was $\sim 10^{-14}$ m$^2$. The scanning speed of the electron beam was $\sim 7 \mu$m/s. During the electron beam irradiation process, the base pressure was kept below $1 \times 10^{-10}$ Torr in order to reduce the effect of adsorption of Fe(CO)$_5$ molecules from the background. In order to form iron silicide locally, the artificial structures on the Si(100) substrate are heated. The process was performed as follows. (1) Fe microstructures are fabricated area-selectively via the electron-induced process of Fe(CO)$_5$, as described above. (2) The substrate is heated via the direct current heating method at a certain annealing temperature for 120 s. (3) The substrate is then cooled to a low temperature (<100 K) again.

An SEM image after the electron-induced process of Fe(CO)$_5$ and after 1190 K annealing are shown in Fig. 2(a) and (b), respectively. In Fig. 2(a), the wire structure is observed only at the electron irradiated position with a width of $\sim 1.6 \mu$m. Note that its width is broadened as compared to the spot size of the electron beam; the present broadening is mainly due to the mechanical vibrations of the sample holder during electron irradiation. The amount of deposited Fe is roughly estimated to be $\sim 20$ ML judging from the relative intensities of Fe MVV and Si LVV Auger peaks. The observed wires exhibit metallic features because they are brighter than the bare Si surface in the SEM image. Fig. 2(b), which is the same scanning region as Fig. 2(a), clearly shows that the artificial structure still exists after annealing up to 1190 K although the contrast becomes weak compared with that taken before annealing.

We performed AES analysis in order to characterize the chemical composition of the artificial structures. Scanning Auger microscopy was performed in this study in order to obtain the local AES signal just at the artificial structures. Fig. 3 shows the Auger intensities of the Fe MVV, Si LVV and C KLL at the wire as a function of the annealing temperature. This clearly shows the vanishing of the Fe signal and enhancement of the Si signal after at 1190 K annealing. The Fe and Si Auger intensities on the wire were almost the same as those on the clean Si(100) surface although the wire structure still exists as shown in Fig. 2(b). These results indicate that the artificial structure is coved by Si atoms. A similar result was reported previously on the annealed iron thin film on the Si substrate [4]. Note that the C KLL Auger peak emerged at 770 K annealing and disappeared after 1190 K annealing. There are two possible reasons to explain the appearance of the carbon. (1) After 770 K annealing, the sample holder was also heated and the CO molecules adsorbed on it were desorbed. Meanwhile, the CO molecules adsorbed on the
surface of the artificial structures, and those on the C KLL Auger peak came to be observed. (2) The carbon atoms segregated from the bulk to the surface after 770 K annealing. The disappearance of the carbon may be due to the diffusion from the surface to the substrate after 1190 K annealing.

The Auger signals clarify significant information relating to the annealed artificial structure. According to the universal curve, the inelastic mean free path (IMFP) of the Auger electrons at 48 eV (Fe MVV) and 92 eV (Si LVV) are 1 nm and 0.6 nm, respectively. Based on these data, the distribution of Si and Fe in depth can be estimated. Since only the Si Auger signal is observed, unlike the Fe MVV Auger signal, the surface of the artificial structure consists of only Si atoms; the iron silicide compound may be buried underneath the Si layer, and the thickness of the Si exceeds 1 nm.

The details of this study have been published elsewhere [5].

References

Fig. 1: The process diagram of electron-induced deposition of Fe. (1) Fe(CO)5 molecules are adsorbed on the Si(100) surface below 80 K. (2) The Fe(CO)5 multilayer is irradiated by a focused electron beam area-selectively. (3) Intact Fe(CO)5 molecules are desorbed by heating to above 350 K. (4) An artificial iron structure is formed at the electron beam irradiating position.

Fig. 2: SEM images of Fe wires on the Si(100) surface. (a) Before annealing, and (b) after 1190 K annealing of 20 ML Fe on the Si(100) (Eg=2keV, I = 0.2 nA).

Fig. 3. The Fe MVV (▼), Si LVV (▲) and C KLL (●) Auger intensities are shown as a function of annealing temperature. Each Auger intensity is measured at the wire center. The range of annealing temperature is from 300 K to 1190 K.
Electron-beam induced deposition in ultra high vacuum: lithographic fabrication of clean iron nanostructures

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The generation of nanostructures with arbitrary shapes and well defined chemical composition is still a challenge and targets the core of the fast-growing field of nanotechnology. One approach is the technique of electron-beam induced deposition (EBID) in which a highly focused electron-beam from an SEM or TEM is used to locally crack e.g. metal containing precursor molecules, resulting in the deposition of the non-volatile fragments.

Up to now, most EBID experiments were performed in high vacuum (HV) environments, resulting in a typical metal content of the corresponding deposits of 15% to 60% (e.g. [1]). The chemical composition (i.e., the purity) of the deposited structures varies with carbon and oxygen being the main contaminations. The carbon contamination of the deposits is attributed to the decomposition of carbon-containing fragments from the precursor gas or of hydrocarbons in the residual gas. In our “surface science” approach we investigate the EBID process under ultra clean conditions to produce high purity deposit structures. For that purpose, we use a UHV system in the low 10^{-10} mbar regime, which allows to minimize contaminations from the residual gas and to prepare a contamination free surface. The central part is a UHV-compatible SEM column, which produces an electron-beam with a diameter of < 3 nm. A hemispherical electron analyzer enables localized Auger electron spectroscopy (AES) and scanning Auger microscopy (SAM) with an ultimate resolution better than 10 nm.

In Fig. 1 two examples of EBID structures generated with our system are shown. The letters “FAU” representing the initials of our institution (Friedrich-Alexander-University) in Figure 1a were produced on Si(111) with the precursor molecule ethene. The width of the lines is partly below 15 nm, which represents the lower limit we can achieve in our system using the “conventional” EBID process, due to a broadening of the electrons in the secondary electron mace.

Surprisingly the EBID deposits from the precursor molecule iron pentacarbonyl, Fe(CO)₅, fabricated at room temperature on Si(001), yield discontinuous structures consisting of individual dots with a size significantly smaller than 10 nm (see Figure 2). The iron content of these dots is estimated to be >95% [2]. Before the onset of the growth of the dot structures the existence of a continuous prerequisite layer with reduced purity was found. A possible explanation for the formation of the clusters is a high tensile stress relative to the initial layer (probably due to lattice mismatch), which leads to a preference for the formation of small clusters due to an overall energy minimization, with some analogy to the Stranski-Krastanov growth mode. This hypothesis was confirmed by experiments performed at 200 K in which the EBID structures are continuous due to the reduced mobility of the involved species. The findings of the present study represent a new route towards the lithographic fabrication of (a) ultra clean nanostructures of arbitrary shape and (b) pure metallic nanodots at defined positions with a size below 10 nm, whose density can be controlled from individual dots to densely packed dot fields with a narrow size distribution.

It is worth mentioning, that the process described above depends on an almost perfectly prepared Si(001) surface. E.g. EBID with Fe(CO)₅ on an Auger-clean but not so well 2×1 reconstructed Si surface (blurred LEED reflexes) leads to rather continuous deposits with a iron content of < 50 %, which is in the range expected for an HV experiment. Therefore, we conclude that at least in this case UHV is not only mandatory to reduce the deposition of molecules from the residual gas but to maintain a well defined surface condition. Consequently, we have demonstrated that our approach to perform EBID in UHV yields novel findings pushing this technique one step further.

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References


Fig. 1: SEM images of two nanostructures generated by EBID. (a) “FAU” pattern on Si(111), obtained with ethene as precursor and the sample at room temperature. (b) Seal structure on Si(111) of the master shown in (c), obtained with trimethyl-methylcyclopentadienyl-platinum as precursor and the sample at room temperature.

Fig. 2: SEM images acquired at RT of two nanostructures (circle and cross) generated by EBID at RT (a) and at 200 K (b).
Ultra-high-resolution electron-beam-induced etching of Si and SiO₂

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Abstract

Critical dimensions in electron-beam-induced processing EBIP are influenced and ultimately controlled by a complex set of interacting variables ranging from electron beam parameters to electron-solid and electron-gas interactions[1-3]. Prior work has been directed toward elucidation of the role of such processes in the field of electron-beam-induced deposition (EBID) as it relates to process resolution[4], but has been minimal in the area of electron-beam-induced etching (EBIE). While very small linewidth (~13 nm) features have been directly written by EBIE into a variety of technologically relevant materials[5], there remains a largely unexplored parameter space for determining resolution-limiting factors including dose dependence and developing surface/feature morphology. In this work, we have investigated EBIE of silicon and silicon dioxide—two of the most important materials to the semiconductor industry—in order to better understand these factors.

The time (or beam dose) dependence of etched linewidth was investigated for both silicon and silicon dioxide and using two different beam energies. Single pixel lines were patterned with a variety of lengths using multiple fast scans (on the order of 1 msec/scan). The dose delivered was calculated as total time per unit length of the pattern so as to eliminate the need to measure the tightly focused beam diameter. Figure 1 shows the results of this experiment, which indicate that for both materials and both beam energies, increased dose results in a general increase in the measured linewidth albeit with a differing functionality. For both materials, there appeared to be a threshold dose for the initiation of etching of at least 2 seconds per micron. Below this threshold, no trench formation was readily observable. Prior experiences with extremely low dose EBIE proved difficult—an effect that we have correlated to chamber cleanliness, where chamber/sample plasma cleaning are critical to limiting the competitive process of carbon deposition from background/sample contamination.

Of greatest interest in Figure 1 is the low dose regime for both materials, where the linewidth is seen to approach roughly the same value in the 10-nm-range. We have attributed this result to the governing of the EBIE process on silicon by the native oxide on the surface. At higher doses, the two materials diverge strongly in the observed linewidth. This is due mainly to the spontaneous etching of silicon by XeF₂ after the protective native oxide is consumed. An interesting observation was that the higher dose silicon lines tend to broaden spontaneously with continued precursor exposure, while the lower dose silicon lines broadened only minimally. It is suspected that this could be due to aspect-ratio-dependent etching (ARDE) as is commonly observed in deep reactive ion etching[6]. ARDE is the process by which conductance limitation in small etched passages decreases the availability of gas species to induce etch reactions at the bottom of the feature, thus reducing the etch rate with time. On the 10-nm scale, it was suspected that this effect may be significant in EBIE and could become a limiting factor on the attainable aspect ratios. Focused ion beam cross-sections did indicate a very low etched depth for the smaller linewidth features, which were as small as 6 nm on silicon dioxide (shown in Figure 2). Figure 3 shows the results of an experiment in which the trench width was varied by defocusing the incident beam to a known diameter at a known beam current. In this manner, the incident electron flux remained constant, while the beam diameter was changed. Therefore, any change in etch rate would be solely due to trench width. Indeed, the observed etch rate increased for larger trench width indicating that conductance-limited precursor flux to the bottom of the trench is a plausible explanation for the minimal broadening of small linewidth silicon and for the poor aspect ratio for both materials at very small linewidths.

References


**Fig. 1**: Effect of line dose on the measured linewidth of EBIE of silicon and silicon dioxide.

**Fig. 2**: SEM image of a sequence of line dose experiments on SiO$_2$. Dose increases from left to right.

**Fig. 3**: The effect of trench width (as determined by spot diameter) on the etched depth of silicon dioxide.
Observation of Coherent Electron Motion in Disordered Granular Metals Prepared by Electron Beam Induced Deposition

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Granular metals are well suited for studying the interplay of four major aspects in solid state physics: quantum size effects, electronic correlations, dimensionality, and disorder. Depending on the preparation technique, one or several of these aspects can be varied to a large degree. In studying these materials electronic transport, which is dominated by inter-grain tunneling, is one important aspect in unraveling the underlying physics. This is so, because the tunnel process is strongly influenced by correlation effects, such as the Coulomb blockade in the limit of weak inter-grain coupling. Only very recently theoretical work on granular metals in the limit of large tunnel conductances, i.e. with a conductivity above a critical conductivity, predicted a temperature-dependent electrical conductivity contribution that stems from the occurrence of a large-scale coherent electron motion between the metallic grains [1].

We measured the temperature dependence of the electrical conductivity of a series of 3D granular metal samples with different metal contents covering the range from insulating to nearly metallic behavior. We prepared the samples employing the technique of electron beam induced deposition (EBID). We observed a $s(T) \sim T^\gamma$ dependence of the conductivity in all of our highly-conducting samples, i.e. those samples which are attributed to the „large-conductance“ regime. We also found the expected stretched exponential behavior $s(T) = s_0 \exp\left((-T_0/T)^{1/\gamma}\right)$ [2] for a highly resistive reference sample attributed to the „small-conductance“ regime with lower metal content. The observed dependencies are in accordance with the predicted interaction corrections deduced for ordered 3D arrays of metallic particles [1]. This implies that the conductance contribution due to coherent electron motion in the low-energy regime is a generic feature of granular metals and is robust in the presence of disorder.

In our experiments we utilized a dual-beam system (FEI, Nova Nanolab 600) with a Schottky-type electron emitter and a ultimate resolution of 1 nm. The precursor gas was tungsten hexacarbonyl W(CO)₆. We used p-doped silicon as substrate material insulated via a 300 nm thick thermally grown SiO₂ layer on which 100 nm thick aluminum contacts had been previously patterned by standard lithography techniques. The samples’ composition were obtained in-situ from energy dispersive x-ray analysis (EDX) at 5 keV electron beam energy.

The conductivity measurements were performed in two- and four-probe geometry at constant excitation voltage in a variable temperature insert mounted in a 4He cryostat. The voltage was chosen such that the corresponding electric field in the samples did not exceed 100 V/cm. In Figs. 1 and 2 an overview of the measured temperature dependent conductivities for samples with different metal content is given. Fig. 1 shows the data for sample #1 having the lowest metal content of 19 at-%. The representation chosen is such that the well-known $s(T) = s_0 \exp((-T/T_0)^{1/\gamma})$ dependence of granular metals in the „low-conductance“ limit is apparent. Such a temperature dependence is due to elastic co-tunneling in the presence of electrostatic disorder [3]. This behavior is not observed for any of the samples with metal content in the range of 27 at-% to 34 at-%. Instead $s(T)$ follows a power-law behavior $s(T) = s_0 + aT^\beta$ over a wide temperature range (from 2 K to 300 K) as shown in Fig. 2. The „large-conductance“ samples all have an exponent $\beta$ very close to ½. Recently such a temperature dependence was predicted by Beloborodov and co-workers based on model calculations for granular metals [1]. They studied correlation effects for a 1-, 2- and 3-dimensional cubic lattice of metallic grains with identical next-neighbor tunnel coupling. These can be classified in two regimes. In the „high energy“ or „high temperature“ regime the granular structure and the grain arrangement is important. Within the lattice model a temperature dependent correction $s_0(T)$ of the conductivity following a logarithmic dependence was obtained [1,4]. It was later shown that this logarithmic temperature dependence is robust against disorder in the tunnel couplings [5]. These theoretical findings now explain experimental data by several groups [2,6]. The „high energy“ correction is expected to show saturation behavior before entering the „low energy“ regime which, we believe, is particularly relevant for the present work. In this regime a dimension-dependent correction $s_0(T)$ is predicted [1]. This correction is analogous to the Altshuler-Aronov interaction correction for disordered metals at low temperature [7]. It signifies a universal character of the large-scale behavior within the granular lattice model. Thus, it is assumed to be robust against disorder, but this has not yet seen rigorous theoretical proof. Beloborodov and co-workers predict in the low-temperature regime
that $s_0(T)$ should follow a $T^{1/2}$ temperature dependence. We assume to have observed this in our experiments. Certainly the most important issue in comparing our data with the model calculation is the high degree of disorder in our samples which was not taken into account in the theoretical analysis. We start with some estimates for the key parameters for the samples. The average bare Coulomb charging energy $E_C$ can be estimated from an averaged grain diameter of 3 nm considered typical for EBID samples. $E_C$ then amounts to about 0.2 eV. The average energy level spacing for the tungsten particles then amounts to about $d = 5$ meV $\ll E_C$, as is required for comparison with the theory. Since we observe the $s \sim T^{1/2}$ behavior in our samples up to room temperature we can specify a lower bound $E_l$ for the upper limit of the „low energy“ regime $E_l = 25$ meV. From the condition $E_l < gd$ we thus estimate the dimensionless tunnel conductance $g > 5$ which would be in line with the necessarily conditions of the theory to be applicable. Nevertheless, it must be stressed that disorder does in fact dramatically reduce the effective conductivity. So, any further quantitative comparison of theory and experiment is not justified. We argue that the observed conductivity should better be considered as a percolating tunnel path between metallic particles or particle clusters. The concept of a percolating tunnel path between particle clusters receives support from two further observations. First, the conductivity does not monotonically increase with metal content but is strongly temperature dependent. Second, irreversible and reversible changes of the conductivities are often observed if the bias voltage is driven beyond a sample- and temperature-dependent critical value. Yet, the temperature dependence of the conductivity of these samples still follows piecewise an approximate $s \sim T^{1/2}$ dependence over an appreciable temperature range. Evidently, the experimentally determined values for $s$ can only be considered as effective conductivities signifying a specific current path along which tunnel percolation proceeds. They are not suitable for estimating the tunnel conductance $g$ relevant for a quantitative comparison with the theoretical prediction.

References


Surface Chemistry and Reaction Dynamics of Electron Beam Induced Deposition Processes

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Abstract

Although electron beam induced deposition (EBID) of volatile organometallic precursors has emerged as an effective and versatile method for creating 2-D and 3-D metallic nanostructures, the range of applications for the deposited materials is often limited by the unacceptably high level of contamination (particularly carbon) present.¹⁻³ To improve control over the deposition process, it is necessary to understand the fundamental molecular level processes associated with electron beam deposition. To address this issue, we have explored the electron beam induced reactions of trimethyl(methylcyclopentadienyl)platinum(IV) adsorbed onto a gold substrate at \( \sim 195K \) under ultra-high vacuum conditions. To simulate the secondary electrons ejected from substrates during high energy electron irradiation, we have employed low energy electrons (40-3000eV) generated from a commercial electron flood gun. Changes in the chemical composition of the film, as well as the gas phase, during electron beam irradiation have been probed using a combination of complementary surface analytical techniques, including x-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), and mass spectrometry (MS).

Our results have shown that the electron stimulated reaction of adsorbed trimethyl(methylcyclopentadienyl)platinum(IV) produces a platinum-containing carbonaceous film. Within this carbonaceous film, platinum exhibits an oxidation state that is intermediate between the Pt(IV) parent compound and metallic Pt (Figure 1(a)). The electron-stimulated conversion of the parent Pt(IV) species to the new Pt species within the carbonaceous film follows first-order kinetics (Figure 1(b)) with a rate constant that is proportional to the electron beam flux. Changes in the surface composition during electron beam irradiation indicates that there is an exact and stoichiometric loss of one of the initial nine carbon atoms of the trimethyl(methylcyclopentadienyl)platinum(IV) precursor during the decomposition process, while IR data obtained in situ reveals that electron irradiation also removes all of the C-H bonds associated with the parent compound. Methane and hydrogen were also evolved during electron beam irradiation of adsorbed trimethyl(methylcyclopentadienyl)platinum(IV). The loss of C-H groups measured by RAIRS as well as the production of gas phase methane and hydrogen (Figure 2) all follow first order kinetics with rate constants that are comparable to the value measured by XPS. These results suggest that a single electron event is responsible for both decomposition of the parent compound and the loss of hydrogen from the adsorbed layer. The measured variation in the reaction rate as a function of incident electron energy was also measured by MS. Results from these studies revealed that the maximum reaction cross-section occurred at an electron energy of \( \sim 150eV \) with a magnitude of \( \sim 1.6 \times 10^{-16} \text{ cm}^2 \). These parameters are consistent with an electron impact ionization process.

In conjunction, the XPS, IR and MS data we have obtained are consistent with the idea that electron stimulated decomposition proceeds via an initial Pt-CH₃ bond cleavage process, mediated by electron impact ionization of the parent compound. The methyl radical that is formed from this step subsequently abstracts a hydrogen atom from the adsorbate layer to produce methane. Such a mechanism predicts the loss of one of the nine carbon atoms from the parent compound, consistent with our experimental observations. Secondary reactions within the Pt complex are assumed to be responsible for the hydrogen evolution. Results from these studies, carried out under well-defined reaction conditions where changes in the gas phase composition and the film’s surface composition can be monitored simultaneously provide new insights into the EBID process. Future studies will focus on means to effect in situ purification of electron deposited materials by controlling the gas phase environment at the growth surface. Towards this end, preliminary results will be presented on the effects that gas phase radicals have on the chemical composition of platinum-containing carbonaceous films.
References


*Fig 1:* (a) Evolution of the Pt(4f) XPS region as a function of electron beam irradiation (500eV, 35μA) illustrates the formation of a new Pt species (Pt\(_{\text{Product}}\)) from the adsorbed Pt(IV) precursor (Pt\(_{\text{Parent}}\)). (b) Kinetic analysis of the XPS data shown in (a) reveals that the conversion from Pt\(_{\text{Parent}}\) to Pt\(_{\text{Product}}\) follows first order kinetics.

*Fig 2:* Mass spectrum showing the evolution of gas phase hydrogen and methane during electron beam irradiation of the adsorbed Pt(IV) precursor.
Measurement of Cross Sections for Low-energy Electron-induced Reactions

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Introduction

It is nowadays widely recognized from experiments on a large number of molecules that low-energy electrons efficiently induce chemical reactions. Secondary electrons that are produced in large numbers when high-energy radiation enters condensed matter [1] or interacts with adsorbates on surfaces [2] thus play an important role in the chemical modifications occuring in the material upon irradiation. This also needs to be considered in the case of electron beam induced processes (EBIP). In consequence, it is not only important to understand and quantify the immediate effect of high-energy radiation on the precusor molecules used for EBIP but also to obtain cross sections for processes induced by secondary electrons.

Our laboratory has recently investigated the potential of different surface analytical methods (HREELS, TDS) for measuring cross sections of reactions induced by low-energy electrons in thin molecular films deposited on solid surfaces. As examples, we have chosen simple organic molecules to demonstrate the viability of the approach [3-5]. Most importantly, we have not only measured cross sections for depletion of the presursors but also for production of different species. The methods and representative results will be summarized in this contribution.

Equipment and methods

The Bremen lab has two separate UHV setups, one equipped with HREELS and sample transfer system, while the other contains a mass spectrometer for thermal desorption spectrometry (TDS) and is linked to an infrared spectrometer for absorption measurements in reflection geometry (RAIRS). Sample cooling to 20 K in HREELS and 35 K in TDS/RAIRS is provided by closed-cycle He crystats. In both chambers vapours can be deposited on permanently installed metal substrates which are cleaned by resistive heating. Deposition of vapours on exchangable substrates is possible in the case of HREELS but at some loss of cooling capability. Electron exposure is performed either by using the electron beam from the HREEL spectrometer or by use of commercial flood guns.

Electron exposure by use of the flood gun results in irradiation of the complete sample surface. Cross sections can thus be determined by measuring the loss of the precursor or the increase of signals ascribed to specific products as a function of exposure. Reference samples are used to quantify the product formation. In the framework of a collaboration with the Université de Sherbrooke in Canada [3,4], we have also measured cross sections by using the HREELS beam for irradiation. In this case, the irradiated surface area must be determined which requires equipment for xy-translation of the sample.

Results

Production of CO from various oxygen containing molecules under exposure to low-energy electrons has been observed. An example is shown in Fig. 1 where CO production from propionaldehyde (CH₃CH₂CHO) is evidenced by the appearance of the lowest electronic excitation of CO in the HREEL spectrum of a thin condensed film of propionaldehyde [4]. Even the low current densities of a typical HREELS experiment can thus efficiently induce the reaction. A cross section for CO formation has been deduced from the integral CO signal and reported in [4].

Exposure of acetaldehyde (CH₃CHO) to electrons at energies above 10 eV results in efficient decomposition of the molecule and production of CO. Cross sections were determined by TDS. At 15 eV the cross section is 2×10⁻¹⁶ m² for loss of acetaldehyde and 7×10⁻¹⁷cm² for production of CO [5]. CH₄ is also produced but the cross section is about an order of magnitude lower than for formation of CO. These values are in reasonable agreement with cross sections obtained previously for similar samples by HREELS. Intermolecular reactions leading to larger products also take place as evidenced by the detection of propionaldehyde.
Outlook

The application of the described methods to cross section measurements for typical precursors used in EBIP appears feasible. The low temperature used in our experiments should allow for a monitoring also of volatile reaction products. On the other hand, particular attention must be paid to catalytic effects by metal deposits produced by decomposing the precursors. Thus, it appears essential to deposit the precursor gas on fresh and well-defined surfaces for each single experiment. Comparing the reaction rate for subsequent intervals of irradiation may give information about additional decomposition reaction pathways opened by the catalytic effect of metal deposits produced during earlier stages of electron exposure. Such experiments are planned for the near future.

References


![Fig. 1](image1.png)

Fig. 1: (a) Electronic EEL spectrum of a four-layer film of PA deposited to a six-layer Kr spacer, recorded during 2 min at \( E_0 = 14 \) eV. (b) Spectrum of same film recorded after 18 min of irradiation with 14-eV electrons (PA\(_{\text{irr}}\)). (c) Electronic EEL spectrum in the range of the lowest-lying triplet state (a\(^3\)T\(_1\)) of CO. The vertical dashed lines show the integration boundaries for determination of the cross sections for the CO production. From [4].

![Fig. 2](image2.png)

Fig. 2: (A) TDS measurements at 16 amu for multilayer films of CH\(_3\)CHO before and after electron exposure of 2000 \( \mu \)C at 15 eV. The magnification is the same for both curves. (B) Plot of the integral peak intensity of the desorption signal at 55 K after exposure, normalized to the intensity of the integral peak intensity at 114 K of CH\(_3\)CHO for the same TDS run, as function of electron exposure at 15 eV and plot of the integral peak intensity of the desorption signal at 55 K in reference mixtures, normalized to the intensity of the integral peak intensity at 114 K of CH\(_3\)CHO for the same TDS run, as function of CH\(_4\) content. From [5].
Focused Ion Beam Induced Processing with the Helium Ion Microscope

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ABSTRACT

The ORION\textsuperscript{TM} helium ion microscope offers high resolution imaging due to a combination of a small probe size (< 0.5nm) and unique beam-sample interactions. The small probe size arises from the high brightness of the ion source, as has been described previously \cite{1}. The imaging behaviour arises in part due to the fact that a primary ion beam in the 10-30 keV range produces only low energy secondary electrons (SE). The electron energy spectrum peaks below 5 eV. With only low energy SE\textapos;s and no backscattered electrons, the technique becomes very surface sensitive. Also, the energy loss for a primary ion beam is at a higher rate than that of an electron beam, and it also peaks at the surface rather than beneath the surface, as for an electron beam. These factors should improve beam induced chemical processing, for the following reasons. It is advantageous to have the SE\textapos;s come from directly under the primary beam impact point, for this localizes the energy provided to induce chemical processes, which should allow smaller feature sizes. Also, having a greater SE yield will provide more energy for beam chemistry. As compared to an electron beam, ion beams have been found to deposit more efficiently \cite{2}. However, the gallium based LMIS microscope has been the standard technology for high resolution ion beam based processing, and this method has several drawbacks. One, gallium is a contaminant that remains in the processed region. Second, the high mass of gallium leads to sputtering which competes strongly with deposition and reduces the chemical selectivity of etching. Third, the brightness of LMIS is low compared to SEM, imposing a limit to the minimum feature size it is possible to write. (Recoiled ions can also broaden the process region in unwanted ways.) Electron beams suffer from a similar problem in that backscattered electrons produce excitations on the surface outside the actual beam landing position, inducing unwanted de-localized reactions. A high brightness helium ion beam should occupy a useful technological space then, having a sub-nanometer probe size, a highly localized, low energy SE emission point, and being largely free of contamination and sputtering. We have a prototype gas injection system in-house to test both deposition and etching in the ORION tool, and we should get preliminary results in the immediate future. We hope to present such results and to discuss our next steps with this technology.

References


Fig. 1: Deposition of a carbon pillar under the helium ion beam. Beam was rastered over a 100 nm square area. Beam current was 0.12 pA, dwell time of 8 μsec/pixel. The resulting pillar retained the square shape of the raster pattern.
Projection Mask-Less Patterning (PMLP) for Nanotechnology Applications

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There are existing and emerging scientific and industrial needs of the reliable and cost-effective fabrication of complex patterns for a large variety of promising nanotechnology applications: (i) nano-imprint templates, (ii) functionalized materials as well as (iii) 2D and 3D surface structures for nano-electronic / magnetic / photonic / biotechnology devices. To fulfill these needs the technique of Projection Mask-Less Patterning (PMLP) is developed by IMS Nanofabrication together with 18 partners within the European project CHARPAN. [1]

The PMLP technology is based on charged particle projection optics with 200x reduction providing thousands of electron or ion beams (H+, Ar+, C60− ...) working in parallel on the substrate (Fig. 1a). As part of the CHARPAN project a PMLP Proof-of-Concept Tool has been realized (Fig. 1b).

![Fig. 1. Principles of Projection Mask-Less Patterning and PMLP Proof-of-Concept Tool, realized as part of the CHARPAN (Charged Particle Nanotech) FP6 project.](image)

Using resolution templates, fine features have been fabricated in a variety of materials with 10 keV Hydrogen ion multi-beam resist exposure (Fig. 2) and Argon ion multi-beam resistless sputtering of material surfaces (Fig. 3).

![Fig. 2. 10 keV Hydrogen ion multi-beam exposure of 20nm HSQ resist at center (left) and edge (right) of the 25μm x 25μm exposure field of the CHARPAN Tool; Exposure Dose: 25 μC/cm².](image)

Inserting a programmable aperture plate system providing ca. 4000 beams, first HSQ resist exposure and resistless patterning results have been accomplished, implementing grayscale exposure techniques. [2]
Fig. 3. CHARPAN Tool results using resolution templates and 10 keV Ar+ multi-beams: resistless 22nm half pitch patterning a) of 70nm Cr on quartz (a), of 25nm MoSi on Cr (b); resistless patterning of Si surface (c) and of GaAs surface (d) and (e).

In 2008 the CHARPAN tool is upgraded with a programmable aperture plate system providing ca. 40,000 beams. In addition, a precursor gas injection system for in-situ ion multi-beam induced etching and deposition is developed and will be inserted. Finally the tool platform will be upgraded with a laser-interferometer controlled vacuum stage to realize a “CHARPAN Engineering Tool”.

Nanotechnology applications of ion multi-beam nanopatterning techniques will be discussed.

References

[1] CHARPAN (Charged Particle Nanotech) is an integrated project of the 6th European framework program (FP6): www.charpan.com

A Modular Ultra-High Vacuum Compatible Gas Injection System with an Adjustable Gas Flow

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Concept

A gas injection system (GIS) heats up an usually powdery precursor and transports the resulting gas through a capillary very close to the focal area of an electron- or ion-beam, which is a necessary condition for the EBID/IBID-process. The designed system is based on the CF 40 vacuum standard and consists of several self-contained components, which are connected via well defined interfaces, so that within some restrictions the parts can be customized or developed further independently. Therefore all scanning electron microscopes and/or every chamber equipped with a focused ion-beam may be upgraded with the created GIS, if a CF 40 flange is available.

The precursor heating occurs inside the vacuum, so that the length of the capillary can be kept short. This allows for a homogeneous temperature distribution, because no extra capillary heating is needed, in order to avoid a negative temperature gradient towards the outlet, which can result in a condensation of the precursor gas. Furthermore, a short capillary guarantees a comparatively high gas flow rate for a given (constant) temperature and the uncontrollable quantity of gas which attains to the recipient after closing the valve is modest. The precursor reservoir is completely surrounded by (actively or passively) heated elements, which again supports a homogeneous temperature distribution. The replacement of a reservoir is done within a few minutes, because of an easy locking mechanism. Moreover, every precursor storage bin is equipped with a valve to eliminate cross contaminations. This means, that different precursors can be simply utilized by using a different bin and capillary. By means of the adjustable valve the gas flow rate can be continuously adjusted in a wide range without changing the temperature. Finally, the reservoir's placement inside the vacuum chamber represents a safety benefit, since possible leaks do not contaminate the environment or endanger the operator.

Components

Fig. 1 shows the complete GIS-system. The main part consists of a central tee-flange with a CF 40 and two CF 16 connections. One of them is occupied by an electrical feedthrough, which provides the heater power and temperature sensor wiring. The precursor temperature is kept constant by means of a pid temperature controller. The valve control, realized via a rotary feedthrough, uses the second CF 16 flange. At the bottom of the tee a guiding pipe has been installed. The heating head, containing the heating unit, the precursor reservoir, the locking mechanism as well as a lateral radiation shield to avoid warming up the electron- or ion-column, is fixed at the end of the pipe. In most cases the available chamber volume is restricted, why the length of the heating head has to be kept short. On the other hand the head's diameter may not exceed 37 mm, because of the CF 40 vacuum standard. This means, that all sub components have to be arranged within a comparatively small volume, which is the primary challenge of the designed GIS. The capillary at the bottom of the heating head is easily changeable, so that different geometries can be tested to optimize the gas distribution step-by-step. Furthermore, the capillary's surface area and its thermal mass are relatively small. This again supports the passive warming, because especially heat loss in form of radiation is reduced.

The remaining CF 40 flange is used to place the tee (including the heating head and the capillary) on a two level motion unit. The first component, the tilt, consists of a compressible metal hose, which is clamped between three threaded rods in each case equipped with a right- and a left-handed thread. Owing to the usage of quick threads, no additional nuts are needed to change the angle of inclination just by screwing the rods. The sensitivity of the tilt mechanism is better than 0,1 mm, and the stability of the preferred setting is supported by the weight of the adjacent linear manipulator. Thus the distance between the capillary and the centre of an electron- or ion-beam can be modified independently from the adjusted inclination. Finally, the motion unit has to be mounted on a recipient-specific adapter flange.
Deposition

For the purpose of testing the designed GIS was attached to a Jeol 6100 electron microscope. A p-doped silicon substrate covered with a SiO₂-layer and the well known precursor tungstenhexacarbonyl (temperature: 54 °C) were chosen. The resulting deposits have been analysed by energy dispersive x-ray analysis (EDX) and atomic force microscopy. In order to study the influence of the beam current on the growing process, deposits with 4 nA to 10 nA beam current were produced, while acceleration voltage (5 kV), dwell time (100 μs) and pitch (20 nm) remained constant. Furthermore, for each parameter set two samples were created to investigate the reproducibility of the process. A maximum variation of 3 at% tungsten content was observed, which complies with the typical EDX-error, if light elements like O and C are quantified. The deposited volume could be reproduced with an error margin of 10%. A second series of samples was prepared with the same parameters as before, but using a twice as high precursor gas flow rate. This resulted in a doubling of the EBD deposition rate measured in μm³/min. For a deposition time of about seven minutes a maximum of 0.98 μm³/min could be realized.

![GIS fixed at assembling unit.](image)

On the right side, the main part of the GIS-system is depicted: A central tee-flange connects the electrical multipin feedthrough, the rotary feedthrough and a guiding pipe, which holds the heating head. On the left, the tilt-unit allows for a regulation of the angle of inclination, whereas the following linear manipulator reduces or enlarges the distance between capillary and the focal area of the electron- or ion-beam. The insert above shows some details of the heating head. The link between the used SEM and the complete system is realized via an adapter-flange.
Multiple-gas-injector for Electron Beam Induced Deposition

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The direct deposition of materials with the focused electron beam has been demonstrated to provide real 3-D structures [1,2] as well as ultrasmall features in the range of a single nanometer [3]. The method of electron beam induced deposition (EBID) is based on the chemical vapor deposition of material initiated by an electron beam induced surface reaction of a precursor molecule. Depending on the type of precursor molecule either metals such as W, Pt, Au, Fe or dielectrics such as silicon oxide have been deposited. However, the purity and the deposition rate are challenging issues when decomposing a precursor molecule. As with conventional chemical vapour deposition (CVD) of blanket layers a potential solution lies in the simultaneous injection of an additional reactive gas.

To facilitate the simultaneous addition of several gases a manually operated gas-injection-system was custom built to allow the introduction of up to 4 precursor gases into the chamber. The system consists of (1) a micro-nozzle system of 3 independent nozzles with a positioning unit and (2) a precursor supply system with precursor reservoirs and gas flow regulators. The gas lines consist of stainless steel and silicone tubing and are also suitable for aggressive media. Reproducible positioning of the gas nozzles is possible by straightforward manual operation of linear stages with a sub 0.1 mm resolution. Nozzle material is chosen to be chemically inert and does not compromise the resolution of the electron microscope.

Using this multiple gas injector system we have investigated the beneficial effects of gaseous additives to several precursor gases. With silicon oxide deposition as additive molecular oxygen has been added to the siloxane precursor, and with iron deposition as additive molecular hydrogen has been added. We have studied the effects of these additives on the material purity, on the deposition rate and on the geometric shape of the depositions. With addition of oxygen to a siloxane precursor not only the deposition efficiency, but also the material purity was significantly increased. With the deposition of iron from Fe(CO)5 the addition of hydrogen gas obstructed the radial growth and led to different geometries.

The addition of a reactive gas species to the primary precursor molecule has the potential to significantly influence the deposited material. This approach has been demonstrated to have a powerful potential for the improvement of EBID-processes.

References


Fig. 1 Gas-injection system for simultaneous addition of up to 4 precursor gases

Fig. 2 Calibration chart of gas flux and resulting chamber pressure

Fig. 3 Influence of hydrogen addition (c,d) on the deposition efficiency EBID of iron structures in contrast to hydrogen-free conditions (a,b). Images show structures deposited from Fe(CO)5 after (a) 30 seconds deposition time without hydrogen, (b) 110 seconds deposition time without hydrogen, (c) 30 seconds deposition time with additional hydrogen, (d) 120 seconds deposition time with additional hydrogen.

Fig. 4 Effect of hydrogen addition on deposition height of Fe-structures deposited from Fe(CO)5. The addition of hydrogen quenches growth of the deposited material.
Optimization of nozzle-based gas injection systems for focused electron- and ion-beam induced processing

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Motivation

For direct-write nanostructuring techniques using focused electron- and ion-beams (FEBs and FIBs) it is crucial to identify the rate-limiting process to understand experimental results, such as the processing rate and resolution [1] and the deposit material composition [2]. One of the fundamental limitations to this objective is the lacking knowledge of the locally supplied precursor molecule flux in most reported studies.

Experimental

In the conventionally used nozzle-based gas injection system (GIS) (Fig. 1a) the molecule flux distribution which reaches the substrate is determined by the nozzle dimensions, its position relative to the substrate and the prevailing gas flow regime. We report on the experimental investigation of the impinging flux patterns on the substrate using a dedicated CVD reactor. The flux distribution is reproduced by the mass transport limited growth rate of the impinging precursor on the heated substrate (Fig. 1b) [3]. Two alternative nozzle designs (Fig. 2) increase the accessible flux to the FEB/FIB up to 6 times for the same molecule throughput injected into the vacuum chamber.

Simulations

Optimization of the local precursor supply by nozzle-based gas injection systems was further investigated based on Monte Carlo simulations of the rarefied gas flow. The ideal position and incidence of the tube nozzle relative to the substrate and the FEB/FIB as well as flux shadowing effects (Fig. 3) are identified.

The results from these investigations provide accurate data of the impinging precursor flux to the processing area in contrast to previous studies [4,5]. The achieved optimization of the precursor supply leads to increased processing rate and resolution while the pressure load for the vacuum system is minimized.

References

Fig. 1: (a) Microscope image of the tube nozzle-based gas injection system (GIS) configuration in side-view. The silicon substrate is mounted on a heating stage to thermally decompose all impinging molecules on the surface. (b) Deposit height profiles determined by optical profilometry (solid lines) deposited from Co$_2$(CO)$_8$ at 200°C substrate temperature with a tube nozzle (d = 400 µm, α = 33°, h = 190 µm). Superposed are Monte Carlo simulations of the normalized impinging flux $J(x)$ in transient flow conditions. The inset shows the deposit topography in top-view.

Fig. 2: Thermal decomposition experiments from the precursor Co$_2$(CO)$_8$ for two alternative GIS nozzle geometries. Microscope images show the nozzle-substrate configuration in side-view. For clarity, the geometry is pointed out by an overlay. (a) Angled tube nozzle. (b) Horizontal nozzle.

Fig. 3: Top-view simulated isoflux contours of the molecular impinging flux on the substrate for a tube nozzle supply (d=400µm, h=100µm, α=33°). The shaded box presents an obstacle of 20 µm height and 10x10µm$^2$ area. Note the shadow effect.
Progressing in FEBIP in a JEOL 6300 F

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Focused electron beam induced deposition [1] and etching [2] process (FEBIP) is a promising technique for nano and micro patterning [3] [4] [5]. It is based on the combination of the injection of volatile chemical compounds (precursors) and electron beam induced chemical reactions in the irradiated region on a substrate. We present here the adaptation of a Jeol 6300F Scanning Electron Microscope (JSM-6300F) for FEBIP. It is a field emission scanning electron microscope incorporating a cold cathode field emission gun, ultra high vacuum, and sophisticated digital technologies for high resolution high quality imaging of nanostructures. Besides the conventional secondary electron (SEM) and backscattered electron (BSE) detectors, the microscope is equipped with an energy-dispersive Xray spectrometer (EDS) microanalysis (Noran System Six). Because of its small spot size at reasonably high currents and low energy, the JSM-6300F is an ideal, thus dedicated research tool for studying physical and chemical FEBIP processes.

For studying FEBIP, a Xenos beam blanker controlled by XENOS XeDraw 2 lithography system has been implemented on our JSM-6300F. The Xenos beam blanker consists of two parallel metal plates mounted in a beamline of the JSM-6300F (Fig.1), acting as a fast beam steering unit (~25 ns), i.e. the time required for the blanking process (from start to finish). During exposure the beam is rastered across the sample and dwelling in selected pixels for a certain time, then rapidly moving on to another pixel. The blanker is needed to prevent the beam from hitting the sample during its relocation to the next position and more importantly to limit the exposure time as short as possible. This has been shown to significantly improve the quality of the FEBIP.

The second part of hardware for FEBIP, is The XENOS XeDraw 2 generator, to write the desired pattern using the electron-beam. It consists of a fast pattern generator (up to 10 MHz) in order to produce the deflection signal data for the patterns which are then written by the JSM-6300F, implementing intelligent writing schemes and shape primitives so as to take full benefit of limited deflection chain bandwidths. When attached to our JSM 6300F, it upgrades the system to perform advanced FEBIP.

A further important unit for studying FEBIP is the gas injection system (GIS). As such a system is not installed on the microscope; an external and internal GIS have been designed and built by our mechanical workshop using stainless steel tubings, and Swagelok connections.

The external GIS is based on a function adapted and modified confiat (CF 48). The designed system consists of a micro-nozzle system with a positioning Kleindiek micromanipulator and a precursor supply system with precursor reservoir and gas flow regulator. For flexible positioning of the micro-nozzle system within the three degrees of freedom (two rotational axes, one linear axis), PFA tubing was used between the micro-nozzle and the tubing systems.

The Internal GIS is designed for injecting a low volatile precursor onto the substrate in the microscope. It consists of a micro-nozzle system fixed to a Swagelok adapter reservoir. The complete internal GIS is attached to the sample holder. The micro-nozzle system must be positioned so that the precursor effusion takes place at 100 μm from the centre of the image. The angle between the micro-nozzle direction and the FEB is selected between 45° to 60°.

First results of FEBIP performances will be presented.

References


Fig. 1: Simplified schematic of Jeol 6300F Scanning Electron Microscope (JSM-6300F) depicting various adaptations for FEBIP applications.
Focused Electron-Beam-Induced Deposition of Platinum at very low Landing Energies

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Electron-beam-induced deposition [1] (EBID) allows the rapid fabrication of three-dimensional nano-devices and metallic wiring of nano-structures within a scanning electron microscope (SEM). The deposited material depends on the precursor chosen; the decomposition of the gaseous precursor is caused by the interaction of an electron beam with a solid substrate. Typical applications of EBID include contacting carbon nano-tubes [2], and growth of tips for field emission [3] and for magnetic force microscopy [4].

The role of secondary electrons in the precursor dissociation process is currently not well understood. We address this by directly investigating depositions created at very low landing energies, down to 10 eV. This energy range has only been explored once before, for tungsten deposition [5]. We have performed EBID of platinum from methylcyclopentadienyl-platinum-trimethyl (MeCpPtMe3) in a scanning electron microscope (SEM) with a focused electron beam whose landing energy was varied from 10 eV to 20 keV (fig.1).

The volume of each deposit was determined by integrating the raw data from atomic force microscopy (AFM) scans. The growth rate of the deposited nano-structures peaks at 140 eV (fig. 2); at this energy the deposition process is over ten times more efficient than at 20 keV. This study provides strong evidence for the dissociation process being primarily driven by the sub-20 eV secondary electrons [6]. We discuss methods for obtaining the adsorbed precursor molecule total dissociation cross-section from these results. Furthermore we demonstrate from energy dispersive X-ray (EDX) results that the composition of nano-structures created with EBID does not vary significantly with electron landing energy between 10 and 1000 eV.

References

Figures

Fig. 1: An atomic force microscopy scan of a successful EBID structure created with a focused electron beam of landing energy 80 eV.

Fig. 2: The EBID deposition yield (nm$^3$ per electron) determined by AFM, as a function of focused electron beam landing energy (eV). The growth rate peaks at 140 eV, where the dissociation efficiency is over ten times that at the more traditional 20 keV.
Electron molecule collisions and plasma modelling using Quantemol-N and Quantemol-P

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Extensive molecular data is a key requirement in understanding modern technical plasmas. One of the fundamental processes in plasma is the collision of low-energy electrons with molecules. For many processes it is difficult to obtain the relevant reliable cross-sections and rates in the laboratory, thus there is an increasing demand for computational procedures to obtain such data.

Here we present two unique expert systems, one for obtaining molecular cross-sections from the study of electron-molecule interactions using the R-matrix method and the other for coupling molecular data with chemical models and a global plasma simulation to enable rapid testing and evaluation of new plasmas.

Quantemol-N [1] is a system designed to make ab initio electron-molecule scattering calculation accessible to the non-specialist. It applies the sophisticated UK molecular R-matrix code, which has proven highly accurate for quantum electron-molecule interactions [2]. By specifying a few easily determined molecular parameters the user can obtain collision cross-sections, excitation cross-sections and rates for electron collisions. Quantemol-N has been used successfully for several target molecules including HCN, HNC, CH 4, CF 2, BF 3, HBr, O 3, C 2H 6 and SiH 4 (see fig. 1).

Quantemol-P [3] is a system for building and running plasma simulations. The user must specify the physical properties of the plasma, for example, power input as a function of time, initial pressure and temperature etc. A set of atomic and molecular species to be considered in the plasma simulation is also specified by the user. The expert system generates a complete set of gas phase reactions and reasonable initial set of surface reactions in a plasma. This set is pruned by discarding un-physical reactions and reaction data not appropriate to technical plasmas (such as auto-detachment). Where data exists, a rate is calculated for the reaction at the plasma temperature so its importance can be evaluated. Where no data exists, a set of heuristics is used (based upon reaction type) to evaluate the reaction's importance. A user can adjust the species, gas phase reactions, surface reactions and plasma properties to control the simulation. The reaction list populated through a database of molecular parameters and cross-sections; missing data can be calculated through molecular cross-sections using Quantemol-N. A zero-dimensional global plasma model (GLOBAL_KIN [4]) is used to perform the plasma simulation. Test studies have been performed for an He/O 2 plasma enhanced plug flow reactor for the production of O 2 -̂ 1Δ and for an SF 6/O 2 deep silicon etch process in an inductively coupled plasma reactor.

References


Fig. 1: Total cross-section for electron-silane collisions. 6-31G Quantumol-N calculations due to Tennyson et al [1].
A study of the surface chemistry and cross sections for electron induced
dissociation for \((\text{CH}_3)_3\text{-Pt-C}_5\text{H}_4\text{CH}_3\) using Temperature Programmed
Desorption

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Introduction

After more than 40 years of research on electron beam induced deposition (EBID) many of the physical phenomena occurring during EBID experiments, such as different growth regimes and the influence of the experimental conditions on the growth, have been studied and are reasonably well understood. Control over the process has developed to the extent that the amount of deposited material can be controlled to sub-nm dimensions, nearly to the level of single molecules \[1\]. However, one important aspect that is not yet well controlled is the purity of the deposits as there is not enough knowledge of the precise nature of the precursor dissociation process in EBID. Therefore, we study the adsorption behaviour of precursor molecules such as \((\text{CH}_3)_3\text{-Pt-C}_5\text{H}_4\text{CH}_3\) and the dissociation cross section as a function of incident electron energy using Temperature Programmed Desorption (TPD) \[2, 3\].

Experimental

The experimental setup consists of an ultra high vacuum chamber (base pressure is \(1\times10^{-10}\) Torr) with a quadrupole mass spectrometer (QMS), a gas nozzle, an Auger electron detector and an electron gun. A Au(110) sample is cooled to about -200 °C, after which the precursor molecules are adsorbed onto it by exposing the sample to a directed flow of precursor gas. Next, the sample is heated at a fixed rate (3.4 K s\(^{-1}\)) and the desorption of the gas is monitored with the QMS. The resulting TPD spectrum shows the temperature at which specific compounds desorb and allows the calculation of the adsorption energies for those compounds. The adsorption behaviour of the precursor molecules can be studied by recording TPD spectra for different surface coverages on the substrate (partial monolayers, monolayers, multilayers).

Results

Fig. 1 shows results of a few TPD experiments. The spectra are recorded for \(m/z = 289\), a fragment of the \((\text{CH}_3)_3\text{-Pt-C}_5\text{H}_4\text{CH}_3\) molecule that contains a Pt atom. The spectrum shows that the first monolayer in contact with the substrate (peak 1) has a higher desorption temperature and a correspondingly higher adsorption energy than condensed multilayers (peak 2). Using the Redhead equation \[4\], the adsorption energy for the monolayer in contact with the Au is estimated to be 55 kJ mol\(^{-1}\). That the adsorption energy is independent of the surface coverage and that peak 2 develops only after the saturation of peak 1, indicate that the adsorption behaviour is first order and that the precursor desorbs molecularly. The precursor desorbs (nearly) completely below 0 °C.

To study the adsorption behaviour in a condition that is more representative for a typical EBID experiment, we deposited a several nm thick carbon/Pt containing layer on the sample by bombarding tens of adsorbed monolayers with electrons. TPD measurements using this “realistic” surface show that the desorption behaviour is similar to that on clean Au(110) (Fig. 2). The peaks have their maxima in the same range of temperatures, although the peaks are wider.

Using this “realistic” C/Pt surface, we studied the effect of electron irradiation on the TPD spectrum. A single monolayer of precursor is adsorbed onto the C/Pt containing layer and subsequently irradiated with a broad beam of electrons. Fig. 3 shows that as the total electron dose increases, the area under the TPD peak for \(m/z = 289\) decreases. This is due to the fact that an increasing fraction of the adsorbed monolayer is dissociated and does not desorb as an intact molecule. Note that a second peak appears at higher temperature. This indicates the formation of a fragment with a higher binding energy. Upon continued irradiation, this second peak also decreases until this fragment does not desorb at all.

The cross section for dissociation can be calculated from the reduction in the total amount of desorbed precursor molecules (i.e. the area under the TPD peak) and the electron dose. Fig. 4
shows the cross section as function of the incident electron energy. The preliminary results indicate that the cross sections of about $10^{-16}$ cm$^2$ are comparable to those for electron induced dissociation in the gas phase. Work will be continued to explore cross sections below 60 eV and above 180 eV.

We acknowledge Howard Fairbrother, Joshua Wnuk and Justin Gorham from the Department of Chemistry at Johns Hopkins University for their useful discussions and cooperation.

References


Overlapping corrections in computation of electron impact various total cross sections for BF\(_x\) (X= 1-3) and BCl\(_x\) (X= 1-3)

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ABSTRACT

Electron–molecule collision cross sections are increasingly important for modeling and controlling discharge environments in low-temperature plasma reactors. The driving mechanism in these plasmas is closely related to general electron–molecule scattering phenomena that occur in the precursor gases during the discharges [1].

In this paper we report computation of total elastic, \(Q_{el}\), total (complete) cross sections, \(Q_T\), for Boron chlorides BCl\(_x\) (x=1-3) and Boron fluorides BF\(_x\) (x=1-3) on electron impact at energies from circa threshold to 2000 eV. We have proposed new model which allows correction resulting due to overlapping of atoms as seen by incident electrons in a complex molecule. The new proposed model gives better results and shows significance of overlapping corrections at low energies. We have employed well known Spherical Complex Optical Potential (SCOP) formalism to evaluate total elastic \(Q_{el}\), total inelastic, \(Q_{inel}\) and total (complete) \(Q_T\) cross sections. Total ionization cross sections, \(Q_{ion}\), are derived from total inelastic cross sections, \(Q_{inel}\), using our Complex Spherical Potential – ionization contribution (CSP-ic) method [2, 3]. Mutual comparison of ionization cross sections for all these targets is carried out in order to have general idea of ionization contribution from individual targets. Present calculations also provide information on the summed total excitation cross sections for these targets. Present results are compared with available experimental [4, 5] and other theoretical data wherever available and overall good agreement is observed.

References:

Computation of electron impact total elastic, total ionization and total cross sections for NFₓ (x=1-3)

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ABSTRACT

The study of dynamics and cross sections of electron molecule collisions form the essential basis for understanding the characteristics of the target molecule [1]. New concepts and advancement of many present-day technologies need the basic knowledge of the wide range of electron-molecule processes and comprehensive information on behavior of electrons in low-temperature plasma. Nitrogen trifluoride is widely used as an efficient fluorine source for the production of very large-scale integrated electronics [2].

In this article we report comprehensive calculations of total elastic (Qₑₑ), and total ionization cross sections, (Qₑᵦ), for Nitrogen fluorides NFₓ (x=1-3) on electron impact at energies from circa threshold to 2000 eV. Spherical Complex Optical Potential (SCOP) formalism is employed to evaluate Qₑₑ and Qₑᵦ. Total ionization cross sections, Qₑᵦ, are derived from total inelastic cross sections, Qᵦₑₑ, using our Complex Spherical Potential – ionization contribution (CSP-ic) method [3, 4]. Present calculations also provide information on the excitation processes of these targets. The calculated cross sections are examined as functions of incident electron energy along with available comparison.

References:

High Precision Gold and Platinum Nanostructures Produced via Focused Electron Beam for Usage in Enhanced Raman Techniques

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Abstract

Recently a new branch of the fascinating field of photonics appeared, called plasmonics. Therein one utilizes the capacity of metal nanostructures to quench light beyond the diffraction limit and enhance electromagnetic fields. These enhancements occur as localized surface plasmon polaritons (LSP) a coupling of the surface density oscillations of the electron gas to the incident light. By varying the parameters of the laser beam which provides the incident photons and the special geometry of the nanoscale rough surface one can reach local electric field enhancement factors in the range of 10^4 which for single molecule detection via surface enhanced Raman scattering (SERS). Raman spectroscopy works with the detection of vibrational modes of chemical bondings and therefore the visualization of their energy levels. This provides the identification of specific molecules based on the chemical fingerprint of the Raman-active bonds [1].

We in our group use the focused electron beam in a dual beam instrument (FEI xP Dual Beam Nova Nanolab 600) for deposition of gold and platinum in carbonaceous matrix based nanostructures from organo-metallic precursor gases. We fabricate high precision nano-needles and pillars with tip diameters down to 10 nm - one option to be used as a reproducible template for SERS. Furthermore we can produce gap-pillar configurations [2] of our high-precision pillars, which allow for the closest gaps on the order of 5 nm between nanostructures in combination with minimized shadowing effects. The smaller the gap between nano-pillars is the higher the electric fields are, if the incident light is adjusted to the geometrical gap and pillar arrangement. Due to the decomposition process of the precursor gases the carbon content in the deposited nanostructures is predominant, forming the matrix in which the metal atoms are dispersed. Plasmonics properties of the deposits are therefore not expected. For this reason, we need to make use of autometallography on the deposits [3], i.e. a chemical process where a reduction of e.g. silver or platinum ions takes place in the presence of reducing molecules. The arising pure e.g. silver layer provides the plasmonically active surface with the designed patterning of the underlying FEB template. Varying the layer thickness of the autometallographical deposit in addition enables a tuning of the plasmonic properties and the influence on the resonant plasmon excitation modes will be tested. To understand the underlying basic physical effects we study nanoshell model systems via finite element simulations. In this simple setup we can shift the LSP resonances due to the ratio of silver shell to dielectric core which can be explained with the model of Plasmon Hybridization [4]. Therefore we hope to make tailored SERS-substrates which are LSP-sensitive to a chosen wavelength and therefore enable the reliable detection of selected molecules.

References


**Fig. 1**: Array of gold-based nano-needles with high aspect ratios deposited via focused electron beam from Dimethyl Gold(III) Acetylacetonate as precursor gas.

**Fig. 2**: Platinum-based gap-pillar configurations with gaps down to 3 nm deposited via focused electron beam from Methylcyclopentadienyl (Trimethyl) Platinum as precursor gas.
Fabrication of plasmonic gold nanostructures by focused electron beam induced deposition

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Introduction

We investigate the use of FEBID to fabricate gold nanostructures on glass substrates for plasmon optics applications [1]. The effects of the substrate material on the structures homogeneity are discussed. Ex situ annealing of the sample is used as a purity improvement method. Scattering optical measurements on the purified dots reveal that they support localized surface plasmon resonances.

Experiments and results

In a first stage, 30 X 30 gold dot matrices with a period of 350 nm were fabricated on silicon substrates. The depositions were performed in high vacuum in a FEI Quanta 200 ESEM equipped with a gas injection system using dimethylgold-acetylacetonate as a precursor. The microscope is interfaced to a Raith Elphy Plus nanolithography system with interferometric positioning. The beam current and the column voltage were fixed at 250pA and at 30kV respectively. By post-annealing the samples in air at 400ºC for 30 minutes the deposition purity is improved due to the elimination of the lesser stable elements (C and O) from the original deposit, leading to a gold purity of 82% wt [2]. Reflection-mode dark-field optical microscopy of the deposited matrices before and after annealing shows a color change from white-blue to yellow-red (not shown). These observations tend to indicate the creation of a selective scattering band associated to the dot’s localized surface plasmon (LSP) resonance.

We then extended our study to transparent substrates which offer further flexibility for optical applications. A gold dot matrix sample was prepared on a glass substrate coated with a thin layer of ITO (Indium Tin Oxide). While SEM imaging on the prepared samples showed well defined dots, low contrast patterns can be observed between them (Fig. 1.a). Transmission-mode Dark-field optical imaging reveals that these patterns, which dominate the scattering image, are actually located below the surface plane (Fig. 1.b). This effect is attributed to a chemical reaction between the acetylacetonate precursor and the oxidized layer of the substrate. With the aim of minimizing this reaction, the deposition was repeated by coating ITO with a 4-nm titanium layer. A weaker effect was thus observed in the optical inspection although it was still significant (Fig. 1.c). Finally, we opt for a bare glass substrate coated by a 4-nm titanium layer. This layer is conductive enough to avoid charge effects and reasonably maintains the substrate transparency. No significant reaction occurred in this case (Fig. 1.d). Scattering spectroscopy under unpolarized light of matrices grown with 8 sec. and 12 sec. dot deposition time was measured after annealing. Eight seconds dot deposition time matrix scattering spectrum features a clear maximum centered at around 600 nm (FWHM of about 80 nm). The 12 sec. deposition time dot matrix scattering resonance is thus found to be red-shifted by about 80nm and significantly broadened (Fig. 2). These results are in good agreement with numerical simulations based on the Green dyadic method, considering pure gold and assuming cylindrical gold dots (Fig. 2).

An increase of the deposition time enables growing gold needles with high aspect ratios. In our annealing process, needles are not bent and their aspect ratio are nearly preserved up to 5:1 (Fourth needle shown in Fig 3; height=1.7μm. width=300nm. before annealing and height=1.1μm. width= 200nm. after annealing).

We are currently investigating the use of FEBID for the growth of gold nanowires. In particular, we studying the influence of proximity effects (Fig. 4 a) described by van Dorp [3]. Repetitive fast scan of each line produces more homogeneity along the deposited lines (Fig. 4 b).
Conclusions

The use of FEBID as a fabrication technique to grow plasmonic gold nanostructures over a transparent substrate has been demonstrated. We have shown that purity and reactivity issues of organic precursors can be partially solved by using a Ti-coated glass substrate combined with ex-situ annealing. The development of this method has been of interest to the nanoscale optics community [4] and opens new perspectives in the fabrication of substantial height/base aspect ratio plasmonic structures.

References


Fig. 1: (a) SEM image of deposited dots on a ITO glass substrate. Dark-field optical images of matrices deposited on different substrates: (b) ITO glass, (c) ITO glass+Ti coating, (d) glass+Ti coating.

Fig. 2: Measured and simulated dot localized surface plasmon resonance for a 8 sec. (diameter:80nm. height:80nm.) and 12 sec. (diameter:120nm. height:80nm.) dot deposition time matrices.

Fig. 3: Growth of tips (a) before and (b) after the annealing process (45º tilt images).

Fig. 4: FEBID of lines using different techniques: (a) single slow scan and (b) repetitive fast scan.
Focused Electron Beam based Production of Nanostructures for optical spectroscopy

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The fast development of the sensor and spectroscopy fields requires new ideas for increasing both the sensitivity of species detection and the spatial resolution of the probed areas. Raman scattering methods can be used for sensitive sensing when putting the analyte in contact with rough at the nanoscale metal surfaces thereby realizing energy transfer to the analyte (surface enhancement - SERS [1]) and/or extremely sharp tips (tip enhancement - TERS). In this way one introduces a signal enhancement due to excitation of localized surface plasmon polaritons (LSP).

We tested different setups for SERS and TERS. First results have been obtained using gold-capped silicon nanowires modified via chemical electroless deposition of silver [2], which is selectively deposited only on the gold caps. Using this surface for SERS we get a signal enhancement factor about 20 times bigger compared to measurements on nanowire substrates without silver amplification. Similar templates with high aspect ratio nanostructures (Fig.1) have been produced with the Focused Electron Beam (FEB) in a FEI xP Dual Beam Nova Nanolab 600 with gold and platinum organo-metallic precursors. Great advantages are the reproducibility in the shape and the regular distribution of the nanostructures on the substrate. They also have been processed with electroless silver deposition by adapting the chemical parameters to the specific carbon rich deposits. Investigations of the influence of the silver layer thickness on the signal enhancement are in progress.

The Raman signal can be enhanced even further using an AFM tip on which a nanowire has been welded [3]. This nanowire serves as external signal enhancer which provides an improved spatial resolution on the order of the tip diameter (50 nm). One can utilize as well FEB produced pillars of different material after silver amplification and therefore benefit from the extremely reproducible and well-defined shape in combination with a tiny tip radius (Fig.2). First results will be presented.

References

Fig. 1: Array of gold nano-needles with high aspect ratios deposited via focused electron beam and Dimethyl Gold(III) Acetylacetonate as precursor gas.

Fig. 2: High precision tip of platinum pillar deposited via focused electron beam and Methylcyclopentadienyl (Trimethyl) Platinum as precursor gas.
Fabrication of Titanium Oxide Nanostructures on Au(111) and Si(111) / Si(100) via EBID

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Nanoelectronic devices, quantum computing and the generation of specific catalytically active structures are only some applications in the fast growing field of nanotechnology. The prerequisite in this field is the generation of nanostructures of high purity and defined shapes. For this purpose electron-beam induced deposition was performed under ultra high vacuum (UHV) conditions in the low 10^{-10} mbar regime. This allows to minimize contaminations from the residual gas and to prepare a contamination free surface. A focused electron-beam (diameter of < 3 nm) from a UHV-compatible scanning electron microscope (SEM) column was utilized. The chemical composition of the deposits was studied by local Auger electron spectroscopy (AES) and AE line scans, while their morphology was analyzed via the SEM.

After the successful generation of clean metallic nanostructures on semiconductor [1] and reactive metal substrates, this contribution focuses on the fabrication of oxidic structures, namely titanium oxide nanostructures on gold and silicon substrates. For the generation of oxidic nanostructures we followed two approaches:

1) selective oxidation of predeposited metallic EBID nanostructures, e.g. FeOx (utilizing the precursor molecule ironpentacarbonyl, Fe(CO)5) on Rh(110);

2) the direct deposition of oxidic nanostructures by utilizing an oxygen- and metal-containing precursor, e.g., TiOx, utilizing titanium isopropoxide [Ti(OiPr)4]; [2] on Si(111) / Si and Au(111).

In the present contribution we focus on the second approach. Whereas the selective oxidation of predeposited metallic nanostructures exhibit basically no contaminations, the use of [Ti(OiPr)4]2 is always associated with a significant amount of carbon as contaminant [3]. However, additional purification of the deposit is possible via different post-treatments. In the case of [Ti(OiPr)4]2/Au(111), the carbon contamination of the deposits could be significantly reduced by an additional sputtering and annealing step (cf. fig. 1). As the titanium AES signal is increased after the treatment, while the corresponding carbon signal decreases, one can conclude that the chemical composition of the deposit in vertical direction is not homogeneous. Carbon seems to cover the deposit, while subsurface layers are of higher purity. For the system [Ti(OiPr)4]/Si(111) or Si(100), the purification of the EBID deposits could be realized by simultaneous heating and oxygen dosage. The formation of pure TiOx nanocrystals with facets on Si(100) was evidenced via AE point scan and SEM images.

Comparison of titanium oxide line deposits on Au(111) and on Si(111), fabricated under similar parameters, shows striking different sharpness. While the deposits on Au(111) appeared to broaden, the line deposits on Si(111) were rather sharp. This occurrence is interpreted as due to different adsorption and diffusion behaviour of [Ti(OiPr)4]. In the case of Au(111), physisorption is assumed, which allows for diffusion of the molecules with a small activation barrier. The assumption of chemisorption of the titanium precursor on Si(111), and therefore a higher activation barrier, which hinders diffusion, would explain the sharper appearance of the line deposits on Si(111). This hypothesis is in accordance with the observation of a higher deposition selectivity on Au(111) in comparison with Si(100) and Si(111) as demonstrated by AES.

Another peculiar finding is the extreme dependence of the shape of the EBID structures on the lithographic parameters. Line deposits fabricated with approximately the same total electron line dose appeared to be sharp (~34 nm), when generated via multiple sweeps and thus short dwell time, and occurred to broaden (~470 nm), when written via one sweep and therefore with longer dwell time (cf. fig. 2). AE line scans perpendicular to the latter lines reveal the elemental distribution of titanium, oxygen and carbon indicating an enhanced electron induced diffusion of mainly titanium as the source for the broadening of the structure.

The diverse experimental findings, possible applications and latest results will be presented and discussed.

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References


Fig. 1: AE spectra acquired on rectangular TiₓOᵧC₂ area deposits on Au(111) (deposit fabricated via six sweeps, total electron area dose of ~10 C/cm², and dwell time of 87.5 μs/nm) before and after a sputtering / annealing procedure with the respective SEM images.

Fig. 2: SEM images of TiₓOᵧC₂ line deposits on Au(111) fabricated with approximately the same total electron line dose. Left side: Broad line fabricated via one sweep, total electron line dose of 32 μC/cm, and dwell time of 8 000 μs/nm. Right side: Sharp line fabricated via ~24 100 sweeps, total electron line dose of ~35 μC/cm, and dwell time of ~0.36 μs/nm.
Novel Approach for the Fabrication and Precise Placement of Optical Antennas

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Here we present a novel approach for the fabrication of optical antennas and their combination with complementary devices such as Scanning Probe tips or optical crystals. Optical antennas are typically Au or Ag nanoparticles in the order of 40 - 100nm of varying shape, which exhibit resonant plasmonic excitation that allow the coupling to electromagnetic radiation in the optical regime. The Near Field created subsequently by the optical antenna exhibits high spatial resolution (as low as 10nm) and impressive intensities [1], allowing to investigate optical properties of matter on unprecedented length scales.

So far, the fabrication of optical antennas was accomplished via e-beam lithography [2] or Focused Ion beam machine [3]. However, implementation and precise placement of an antenna on top of other devices such as a Scanning Probe tip is very difficult. This motivated the development of an alternative approach, allowing the precise placement of uncontaminated, reproducible and shape determined Au optical antennas. Therefore, a W mask was deposited using electron beam induced deposition [4] on a 40nm Au film and differential low-energy ion milling was employed to transfer the shape of the mask to the gold, resulting in well defined Au nano particles. This method enables the implementation of a large variety of shapes. Here, we present the realization of bowtie - like optical antennas [2], formed by two opposing triangles with a gap between their tips of 5-15nm. This specific shape exhibits promising properties, specifically for Near Field optical devices [1,3].

The electron beam deposition was carried out using a Zeiss cross beam. The electron beam energy was 20 – 30kV, producing spatially confined secondary electrons around the incoming beam, which dismantle the W precursor (W-). The shape of the mask is controlled with a XENOS pattern generator enabling a variety of possible shapes. Subsequently, the masks were etched with 80W Ar+ plasma for few seconds to dry etch part of the W mask, specifically small W residues surrounding the actual mask. This was followed by a 30W etch, taking advantage of the different etch rates of Au und W, resulting in free standing well defined Au bowtie optical antennas. This work was performed at the Molecular Foundry, Lawrence Berkeley National Laboratory, and was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02—05CH11231

[1] Improving the mismatch between light and nanoscale objects with gold bowtie nanoantennas, Schuck PJ, et.al., PRL 94, 017402, 2005


Electron-beam Induced Deposition and differential dry etching to build plasmonic nanostructures

Figure 1 a) Process procedure overview. b) Array and close up of bowtie masks, individual triangles have a base of 83nm, are 75nm high and exhibit a gap size of approximately 10nm. c) Au bowties after etching process illustrated in a): the gap size is about 10 nm. d) Precise placement of a bowtie on an FIB cut AFM tip, demonstrating the capabilities of this novel method.
Chemical Lithography: FEBIP with SAMs

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Chemical lithography is a resistless electron beam induced process that creates chemically defined, high resolution surface nanopatterns in self-assembled monolayers (SAMs). SAMs are films of amphiphilic molecules, covalently anchored to a solid surface (Au, Si, SiO,...). When SAMs are exposed to electrons, the molecules react in a very specific manor. In organic molecules, electrons break C-H bonds. In aromatic SAMs, such as biphenyl or terphenyl, the C-H cleavage is followed by a lateral cross-linking of neighbouring molecules, resulting in a stable monomolecular film [1]. Cross-linked aromatic SAMs show high mechanical strength and stability against etchants [2-4]. They are thermally extremely stable and withstand temperatures above 1000 K in vacuum [5]. The cross-linked films can even be released from their supporting surface to form freestanding carbon nanosheets [6] with a thickness of only ~1 nm. A technical application of carbon nanosheets is their use as ultrathin supports for transmission electron microscopy [7]. We tested their applicability by imaging nanoparticles on nanosheets. The corresponding electron micrographs show significant improvements over those made with conventional carbon films.

When nitrobiphenyl SAMs are exposed to electrons, the released hydrogen reduces the terminal nitro functionality to amino groups [8]. Hence e-beams generate cross-linked and amino generated regions. Due to this change of the chemical functionality, other molecules can bind to the amino groups [9]. This creates chemical surfaces pattern that can be used to the surface immobilization of different molecules. It has been shown that, among others, polymers [10], dyes, and proteins can be attached to amino terminated surfaces. The reversible immobilization of functional proteasome proteins [11] is presented and discussed, as it represents a first step towards a FEBIP based fabrication of a biochip.

References

Electron Beam Induced Deposition of Platinum-Containing Structures at Cryogenic Temperature

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Abstract

Electron beam induced deposition (EBID) of platinum-containing materials was performed at cryogenic temperatures. Deposit morphology, microstructure and nanostructure have been characterized by scanning and transmission electron microscopy (SEM and TEM), and shown to be controllable by the electron fluence used for EBID.

Experiments were performed using an FEI Nova Nanolab 600 SEM-focused ion beam system with a LN₂ cryogenic stage, which enabled the substrate to be cooled to -150°C. A gaseous platinum precursor (MeCpPtMe₃) was first condensed onto the cooled substrate using a capillary-style gas injection system (GIS) [1]. Next, gas flow was terminated and the condensate was irradiated with the electron beam to induce precursor decomposition. The thickness of the condensate was controlled by lowering the stage to increase the distance to the GIS needle to as much as 1 mm. When the substrate was returned to room temperature, any unreacted precursor desorbed and was removed by the pumping system, while irradiated regions show clear evidence of successful deposition, as illustrated in Fig. 1. The morphology of the deposited material depends on exact deposition conditions, and exhibits several distinct types absent from deposits made by conventional (room temperature) EBID.

Figure 1 shows a deposit made by varying the electron fluence, through decreasing the microscope magnification in a step-wise fashion. Distinct columnar, smooth and mesh deposit morphologies were observed as a result of the changes in electron fluence. Figure 2 shows a FIB cross-section of a columnar film, while Figs. 3 and 4 illustrate a smooth and mesh morphology, respectively. To further elucidate the role of electron fluence on the morphology and quality of cryo-EBID films, experiments varying the total number of scans, magnification (scan area) and beam dwell time were performed using a beam energy and current of 15 keV and 0.58 nA, respectively. Figure 5 summarizes the correlation between electron fluence and observed film morphology. These preliminary results fall into several well-defined fluence regimes, which suggests that electron fluence offers a simple means for controlling the resultant morphology of the deposit.

To investigate the composition of the deposited material, Auger Electron Spectroscopy (AES) and Energy Dispersive X-ray Spectroscopy (EDS) were used. EDS indicates the presence of carbon, platinum, oxygen and silicon (substrate), while AES analyses of deposits made with a 15 keV electron beam were found to contain 35-45% platinum with the remainder being carbon. Oxygen concentration was negligible with respect to the noise in AES. Thus the O signal in the EDS spectra is assumed to be surface oxidation rather than a bulk contaminant. To examine the interior microstructure of the cryo-EBID material, TEM specimens were prepared by depositing a platinum mesh directly onto holey carbon grids. Figure 6 is a high-resolution TEM micrograph showing the deposit consists of ~2 nm platinum particles imbedded in a carbonaceous matrix. Evidence of electron annealing in the TEM during observation and the implications for the stability of the structure will be discussed.

References

Fig. 1: Cryo EBID deposited platinum with columnar, smooth and mesh morphology. The columnar region corresponds to irradiation between 65-10KX magnification, the smooth region between 8.5-6KX and the mesh region between 5-2.5KX.

Fig. 2: SEM cross-section of a columnar platinum film illustrating high electron fluence effects on deposition morphology.

Fig. 3: Smooth platinum film morphology and cross-section.

Fig. 4: Platinum mesh grown at low electron fluence.

Fig. 5: Correlated electron fluence vs. experimentally observed film morphology.

Fig. 6: TEM of platinum mesh deposited on a holey carbon grid. Pt ~2nm particles (dark) are embedded in an amorphous carbon matrix (light).
Development of a Liquid Precursor and a Deposition Process for Carbon and Chlorine Free Direct Writing of Gold

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Introduction

Metal containing precursors are used in several important technological applications for structuring on the micro and nano scale. Especially gold containing precursors are very interesting because of good electrical, mechanical and chemical characteristics of gold structures and layers.

Most precursors for FEBID of gold or gold containing depositions found in literature are metallo-organic compositions, i.e. Au(CH3)2(acac) (acac = acetyl-acetonate), Au(CH3)3PF3, CH3Au(P(C2H5)3) and other derivatives [1]. As carbon free precursors mostly HAuCl4 and AuClPF3 are used. All these precursors have in common, that depositions of them contain carbon or chlorine in non-negligible amounts which influence the properties of the resulting depositions in comparison to bulk gold material in a negative way.

In this work we present the results of the development of a novel precursor and a corresponding process for the electron beam based direct writing of carbon and chlorine free gold lines and dots.

Precursor

The precursor was developed in the institute of pure and applied chemistry at the University of Oldenburg. The synthesized chemical compound used for the line depositions in this work is (NO2)[Au(NO3)4] which is solvable in N2O5 and can be dissociated under electron beam irradiation or thermal influence. In comparison to conventional precursors for gold deposition, all dissociation products of our precursor except of gold are gaseous. Measurements with DTA/TG, DSC, TDS and XPS showed a different behavior under thermal and electron beam induced decomposition, in each case with several intermediate states but in both cases the chemical reaction results at least in high concentrated gold.

Direct Writing Process

At room temperature, the developed precursor comes in a liquid state with a low vapor pressure. Because of its physical properties it isn’t possible to evaporate it or to inject it in a gaseous state as usual in most electron beam induced processes. Instead, the precursor solution is applied with a spin coating process as a thin film directly onto the desired surface, i.e. a silicon wafer. The desired structures can now be written with the electron beam into the precursor layer whereby the irradiated areas react to a solid gold deposition. This process is comparable with classic electron beam lithography but with direct structuring of the gold material instead of a resist layer. The non-structured precursor can be rinsed after completing the structuring step. Fig. 1 shows the three major steps of the process. A similar process based on a Au55(PPh3)12Cl6 precursor is known from [2]. However, this process uses ion beam writing and the precursor contains chlorine.

Results

Fig. 2(a) shows line depositions made with the developed precursor and deposition process. The lines were made in a tungsten cathode SEM “FEI QUANTA 600” in a precursor layer of several hundred nanometers thickness and were written with an electron beam accelerated to 20keV at a beam current of 1.2 nA. Fig. 2(b) and (c) show an AFM image of the ends of three deposited lines and a corresponding height profile. This shows a line width of about 1.5μm and a line height of 80nm in the line center, whereby the line edges are up to 60nm higher. This characteristic shape can be attributed to a volume reduction of the precursor during the decomposition.
References


1. Application of the precursors onto the substrate (spin coating)

2. Decomposition of the precursor with the electron beam

3. Rinsing of the non-reacted precursor with water

Fig. 1: Schematics of the steps for the direct writing process of gold with the electron beam.

Fig. 2: (a) optical microscope image of deposited gold lines; (b) AFM image of a detail of (a); (c) height profile of a deposited line as marked in (b).

Fig. 3: EDX mapping of a line end (left) as a detail view of the SEM image (right). Yellow indicates gold. Lines deposited with the developed precursor and deposition process.
Analysis of Resist Shrinkage by Electron Beam Irradiation

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Experimental results and Analysis with Monte Carlo Simulation

Resist polymers are known to shrink or swell during electron beam (EB) irradiation. It is well known that the shrinkage of resists for argon-floride-excimer laser (ArF) by EB exposure is serious, and the minimum dose is required for the measurement by critical dimension (CD) scanning electron microscope (SEM).[1] In a process of EB direct write lithography the deformation will occur locally depending on a pattern during the exposure, and an attention should be paid for the CD control. Mechanisms of the deformation so far known are (1) evaporation of its solution by local heating, (2) molecular chain-scission and cross-linking by radicals excited by EB, (3) mass loss of resists by evaporation, etc.

Figure 1 shows a cross-section of poly-methyl-methacrylate (PMMA) board of 1.5 mm-thick after EB irradiation and cleaved perpendicular to the line exposed. 40nm-thick Al film has been evaporated on the PMMA to avoid charging problems. The beam energy is 20keV and the current is 1nA, and the dose is 900nC/cm. Just below the EB incident point, the surface is quite smooth with a little radial pattern. There is a clear boundary, and a radially expanding streak patterns are observed at the outside. According to our numerical calculation of heating of the resist based on a Monte Carlo (MC) simulation of electron trajectories, the maximum temperature rise is less than 10 degree in this case, and it is not possible the deformation is attributed to its heating. The pattern found at the cross section agrees well with the equi-energy deposition contour shown in Fig. 2 obtained by our MC simulation of electron trajectories described above in the resist.[2] Then it is expected that the deposited energy and the shrinkage should be strongly related.

The shrinkage of PMMA film of 1.4 \(\mu\)m-thick on Si substrate by 15keV EB has been studied by Koval[3] in a wide range of exposure doses from about 4 to \(10^5\) \(\mu\)C/cm\(^2\). As it is well-known, in a common EB lithography with PMMA, the doses necessary are around 100\(\mu\)C/cm\(^2\), the maximum dose given there is huge. Using our MC simulation of electrons, the Koval's result is converted to a relation between the microscopic shrinking distance and the deposited energy density. As the result, it is now applicable to any incident energies of EB and any thicknesses of PMMA to obtain the final macroscopic dent distance of surfaces by the summation of all local shrinking distances. Here, we assume 5 nm-cells in lateral and vertical direction, and the displacement of the center position of the cell is simulated in both directions. In the same exposure condition of Fig.1, the displacement of the point in the cross sectional view is demonstrated in Fig.3, where those positions of points at the outer boundaries (+/-10\(\mu\)m in lateral, and +10\(\mu\)m in vertical) are fixed. The central opening of the array points means the presence of the tensile stress in the material, and a crack is actually observed in Fig.1. The maximum dent found below the EB incident point in Fig.1 is about 1\(\mu\)m, and it agrees well with that is shown in Fig.3, and the correspondence between the deposited energy and the amount of shrinkage seems to be successful.

For more quantitative analysis on the amount of the shrinkage, we expose a square pattern of 50\(\mu\)mX50\(\mu\)m for different PMMA thicknesses and EB parameters, e.g. energy and current. Figure 4 shows a process of the experiment. Without covering the 1\(\mu\)m-thick PMMA film on Si substrate by conductive material, EB is exposed, and just after the exposure the depth of the surface dent is measured by an atomic force microscope (AFM). Figure 5 shows the results for doses ranging from 1000 to 20000\(\mu\)C/cm\(^2\). As shown in the figure, the depth obtained by 20keV EB is larger than that by 30keV EB. According to our MC simulation, the ratio of deposited energy of 20keV EB is about 1.65 times larger than that of 30keV EB in 1\(\mu\)m-thick PMMA, and it is close to the experimental result, as the dose is at 1000-2000\(\mu\)C/cm\(^2\). However, the ratio decreases rapidly with increasing the dose. This phenomenon suggests that the shrinking process saturates in such high doses, and the amount of the shrinkage does not show a linear function of energy deposited. Figure 6 shows the EB current dependence of the shrinkage. It is peculiar that even if the dose is the same, the depth of the surface dent exposed by the lower current EB gives the larger values, and this is also found for 30keV EB. Although it is not fully understood, the reason might be that the shrinkage is based on a slow mechanism, such as mass loss of resist by evaporation, and if EB incident rate is too high, the shrinking efficiency decreases. In such a high dose condition, the deposited energy can no more be a practical measure of the shrinkage. In the workshop a tentative model will be given for the phenomena.
Fig. 1: Low voltage (1kV) SEM image of the cross sectional view of PMMA irradiated by 20keV EB at a line dose of 900nC/cm. The dose is realized by multiple line exposures. The original surface is covered by Al film of 40nm-thick, but it is disappeared during the exposure.

Fig. 2: Equi-energy deposited contours obtained by MC simulation, considering cascade multiplication of secondary electrons in PMMA. The scale is set to agrees with the picture shown in Fig.1. In usual EB lithography, the contour of around $1 \times 10^{21}$eV/cm$^3$ is apparered after development process.

Fig. 3: Simulated bulk shrinkage of PMMA. Every point in the figure shows a center position of an allocated cell. Based on Koval’s data of shrinking ratio of the film with the exposure dose, the shift distance of local cells is simulated. The depth of the surface dent at the EB incident point agree well with experimental result shown in Fig.1.

Fig. 4: Experimental procedure to clarify the shrinking process. Depth of the dent made by areal exposure of EB is measured by AFM. Dependence of the shrink is studied in a wider variety of parameters of PMMA films, EB doses, energies and currents.

Fig. 5: Depth distribution of dent made by areal exposure of 20 & 30keV EBs, as a function of the dose. Ratio of the depth decreases rapidly with increasing the dose.

Fig. 6: Depth distribution of dent as a function of the dose for various EB current. As the current is small, the depth of the dent is large, even in the same exposure dose.
Tunnel Percolation and Current Path Switching in a Granular Metal

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Model of Percolation

A simple model for studying percolation is that of a regular lattice of sites which are occupied by atoms with a probability $p \leq 1$. For current transport to occur from "top" to "bottom" at least one continuous path of occupied lattice sites (current path) is needed. This percolation model can be translated into granular metals, if the atoms are replaced by nanocrystallites. The current transport is now depending on the tunneling probability between the crystallites.

Experimental Results

For sample preparation we utilized a dual-beam sytem (FEI, Nova NanoLab 600) with a Schotky-type electron emitter and a ultimate resolution of 1 nm. The precursor gas was tungsten hexacarbonyl $\text{W(CO)}_6$. We used p-doped silicon as substrate material insulated via a 300 nm thick thermally grown $\text{SiO}_2$ layer on which 100 nm thick aluminum contacts had been previously patterned by standard lithography techniques. The samples’ compositions were obtained in-situ from energy dispersive x-ray analysis (EDX) at 5 keV electron beam energy.

We have prepared a series of strip-like granular metals consisting of tungsten nanocrystallites embedded in an insulating matrix by means of electron beam induced deposition (EBID). The metal content varied between 19 at-% and 34 at-%. In this metal content range the existence of a direct percolation path between $\text{W}$ nanocrystallites can be safely excluded. The samples have been analyzed by voltage-current and temperature-dependent conductivity measurements. Within the insulating matrix the nm-sized metallic nanocrystallites are irregularly distributed. The samples have been measured in standard 4-probe geometry. We observed current flow in all of our samples, which one would not expect within a simple percolation model, yet several experimental observations suggest that percolation effects, possibly between clusters of nanocrystallites, have a role to play in these materials. We suggest a tunneling percolation model that may explain some characteristics of our EBID samples, as the switching of the current paths for activation and reparation of “destroyed” samples and the observation of enhancements of the conductance of selected samples by a factor of $10^6$.

In Figure 1 a typical voltage-current characteristic is shown. In the left inset of Fig. 1 a voltage sweep of 1 V was applied to the inner contacts of the sample. After achieving a current flow of 250 $\mu$A a rapid decrease of the current was observed. This would seem to imply an irreversible destruction of the sample. However, the voltage-current characteristic measured on the outer contacts of the sample after this irreversible change observed on the inner contacts showed a significant current flow. This suggests that the sample is neither destroyed nor can the current flow be homogenous across the sample cross section. Arguably, within the tunnel percolation model the current path simply switched. By increasing the voltage and providing more energy for the electrons another current path was found. This is shown in the main graph of Figure 1. At about 4 V the current increases strongly. The smaller jumps in the characteristic do not cause a stable change of the current path. Within our experience a current increase of at least three orders of magnitude yields to a stable current path. The right inset of Fig. 1 shows the voltage-current characteristic after achieving a new current path. A voltage up to 0.1 V now results in a current in the $\mu$A regime.

Figure 2 shows the voltage-current characteristics of an EBID sample which is apparently badly conducting. The left inset shows the I-V-curves of the deposit in its original state. For comparison the I-V-curve as measured between blank contact pads is also shown. This gives an indication of the isolation resistance of the $\text{SiO}_2$ layer. The main graph depicts the irreversible “activation” process by increasing the voltage beyond the sample-specific critical voltage $V_c$. A new current path is formed. The small peaks in the three curves are an indication for spurious path switching processes. The right inset depicts the voltage-current characteristic after the deposit
has been “activated”. If compared to the original I-V data it can be observed that the conductance has increased by a factor of $10^5$ at 0.1 V bias.

**Fig. 1:** Reparation of an apparently destroyed sample

**Fig. 2:** Activation of an apparently poorly conducting sample
Superconductivity of Nanoscale Tungsten Grown by Focused-ion-beam Deposition

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Abstract

Amorphous tungsten films [1] and alloys [2-4], when rendered into a disordered or granular state, can have a superconducting transition temperature \( T_c \) up to two orders of magnitude larger than that of single-crystal bcc tungsten. It has been reported that focused-ion-beam (FIB) deposited tungsten was superconducting with a \( T_c \) of 5.2 K [5-6]. However, the mechanism behind the significantly enhanced superconductivity of such materials is not clear. Can the superconductivity of FIB-deposited tungsten be tuned by varying the growth parameters? Can we exploit the three-dimensional (3D) fabrication possibilities offered by FIB to make freestanding superconducting nanowires? To understand the answers to these questions, we have used FIB to grow tungsten nanostructures with tungsten hexacarbonyl \( \text{W(CO)}_6 \). Vertical nanorods and “flying” 3D tungsten with cross-sectional diameter of order 100 nm were grown with a 1 pA gallium ion-beam current. Lateral tungsten nanowires were deposited in the four-terminal contact configurations with various ion beam currents, ranging from 1pA to 1 nA with a constant ion fluence. The temperature dependent electrical properties have been studied for both the flying and lateral nanowires.

References

Transport properties of IBID and EBID Pt nanodeposits

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Introduction

Ion-beam-induced (IBID) and electron-beam-induced (EBID) Pt nanodeposits are widely used in many applications in the fields of microelectronics, nanotechnology, electron microscopy, etc. In this contribution we focus on the transport properties of IBID and EBID Pt nanodeposits grown in a dual beam equipment (Nova 200 Nanolab by FEI) using (CH3)3Pt(CpCH3) as the metal-organic precursor. These experiments are relevant for applications where the resistivity and the bias voltage dependence of the resistance of the IBID and EBID Pt nanodeposits play a role.

Experimental details

Optical lithography techniques have been used to pattern Al microelectrodes on a Si3N4 (300 nm)//Si substrate. The mask design leaves a 12 μm gap between the microelectrodes, which is filled in with the IBID or EBID Pt nanodeposit. Electrical microprobes for in-situ control of the deposit resistance have been used. These conductive microprobes are connected via a feedthrough to a multimeter located out of the dual beam chamber, which allows measuring the deposit resistance in real time by two-probe measurements with negligible lead resistance (about 13 Ω) as shown in figure 1. Another mask design for in-situ four-probe measurements of I vs V properties has been realized. In that case, a combination of a current source and a nanovoltimeter have been used for precise electrical measurements.

Results and conclusions

As shown in figure 2, the resistance of the IBID Pt nanodeposits decreases fast with deposition time, reaching values in the range of a few KΩ after a few minutes. The final resistivity is about two orders of magnitude larger than in the case of pure Pt, which is consistent with the existence of a substantial carbonaceous matrix in the deposit. The resistance of the EBID Pt nanodeposits decreases smoothly with deposition time, reaching values in the range of a few MΩ after a few minutes. This indicates that the resistivity of EBID Pt deposits is definitely several orders of magnitude larger than their IBID counterparts. This large difference can be attributed to the significantly different composition and microstructure of the IBID and EBID Pt deposits [1]. In-situ I vs V curves of the IBID and EBID Pt nanodeposits shown in figure 3 give evidence for the different transport mechanism in each case. Whereas the IBID deposits show a linear dependence as expected in metallic conduction, the EBID deposits present strong non-linear behaviour, as expected if the conduction is governed by the amorphous carbonaceous matrix [1, 2]. The ex-situ study of the resistance versus temperature in these deposits confirm the different transport mechanism in each case. The systematic study of the transport properties of IBID Pt nanodeposits as a function of the deposit thickness shows a rich phenomenology [2].

References

Fig. 1: The image on the left is a SEM picture of the Al electrical pads patterned by optical lithography together with the two microprobes contacted for in-situ control of the deposit resistance. The image on the right is a SEM picture of one typical deposit closing the gap between the contact electrodes for the measurement of the nanodeposit resistance.

Fig. 2: The shown results of resistance versus time correspond to the comparison between an EBID and an IBID Pt deposition. In the case of the shown EBID deposit, we have used the conditions: beam current=0.54 nA, beam energy=10 keV, dwell time=1 μs to reach after 15 minutes a final thickness and resistance of 160 nm and 22.3 MΩ respectively. In the case of the IBID deposit shown, we have used the conditions: beam current=10 pA, beam energy=30 keV, dwell time=200 ns to reach after 11 minutes a final thickness and resistance of 160 nm and 1 kΩ respectively.

Fig. 3: I vs V curves taken in-situ by means of 4-probe measurements of an IBID Pt deposit of resistance about 1 kΩ and an EBID Pt deposit of resistance about 50 MΩ. In the case of the IBID Pt nanodeposit the response is linear whereas it is non-linear in the case of the EBID Pt nanodeposit.
Introduction

EBID and IBID of materials is a chemical vapor deposition (CVD) induced by focused electron- and ion-beam, respectively. The model proposed to explain the EBID is that primary, backscattered and secondary electrons can dissociate precursor gas molecules on the substrate [1]. For IBID, the collision cascade model can explain the decomposition of the adsorbed gas molecules on the substrate [2]. Previous studies on EBID Pt deposits have shown the decrease of the deposition rate as a function of the beam energy [3,4]. However, in the case of IBID Pt deposits, the deposition rate was found to vary little [3,4]. The composition and microstructure of the Pt deposits have been studied by means of energy-dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM) [3,5]. These studies showed that the deposits consist of Pt-rich inclusions in a carbonaceous matrix. In this contribution we present a systematic study of the composition, volume per dose, and microstructure of EBID and IBID Pt deposits as a function of the beam energy and current [6].

Experimental

Our experiments were performed in a dual beam equipment (Nova 200 NanoLab). The composition was measured by means of an EDX detector (Oxford Instruments). The volume per dose was calculated after performing cross-sections of the deposited material measuring the deposit thickness. Finally, the microstructure was investigated by TEM (JEOL 1010, 200 kV).

Results and conclusions

The atomic Pt content in EBID decreases as a function of the incident electron-beam energy as shown in fig.1a), whereas the volume per dose (EBID) dramatically decreases by a factor of four as illustrated in fig.1b). This can be explained by the decrease in the amount of secondary electrons reaching the sample surface. For IBID, the atomic Pt content also decreases as a function of the incident ion-beam energy whereas the Ga content is quite constant as shown in fig. 2a), which was related by the sputtering rates. However, the volume per dose for IBID increases as illustrated in fig. 2b), which would be explained by the slight changes in the energy dependence of the secondary electron yield. The microstructure study of the EBID Pt deposits show independent Pt nanocrystals with a narrow site distribution centered around 2.5 nm embedded in an amorphous carbon matrix (see fig. 3a)). On the other hand, in the IBID Pt deposits, we find Pt nanocrystals with a broader site distribution and tendency to percolation as shown in a fig. 3b).

References

We kindly acknowledge the experimental help and discussions with Dr. J. Arbiol (Serveis Cientifico-Tecnics, Universitat de Barcelona), Dr. J. Sesé and L. Serrano.

Fig. 1: a) Average Pt atomic content (measured by EDX) versus incident electron beam energy in the investigated EBID deposits; b) Average volume per dose versus incident electron beam energy in the investigated EBID deposits.

Fig. 2: a) Average Pt atomic content (measured by EDX) versus incident ion beam energy in the investigated IBID deposits; b) Average volume per dose versus incident ion beam energy in the investigated IBID deposits.

Fig. 3: HRTEM images of an EBID Pt deposit a) and an IBID Pt deposit b. Insets are the FFT of platinum nanocrystal domains.
Stiffness, density and quality of high aspect ratio Cu/C nanostructures produced by focused electron-beam induced deposition

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Motivation

With their maskless direct-write nanofabrication capabilities focused electron-beam (FEB) techniques will become increasingly important for device prototyping applications. Gas assisted FEB deposition and etching is used as an attach-and-release tool in electron microscope based nanomanipulation of individual nanostructures as well as a tool for functionalization of AFM sensors. In view of these applications, characterization and control of the mechanical properties of FEB deposits is becoming a major issue.

FEB deposits often feature a composite structure, i.e. nanocrystalline (metal) grains embedded in a carbonaceous matrix. Evidently, the mechanical properties, such as stiffness, toughness, and adhesion must be determined experimentally since no data is available from template bulk materials.

Experiments and Results

From the combination of bending tests using in situ cantilever-based force sensing (Fig. 1) and modal vibration analysis (Fig. 2) we deduced Young's moduli and densities of FEB deposited pillars from the precursor Cu(hfac)2. From several pillars deposited at 5 keV and 20 keV primary electron energy and otherwise equivalent conditions the average Young's modulus was 16 GPa and 25 GPa and the corresponding densities 1.9 g cm⁻³ and 3.9 g cm⁻³, respectively. The measured density values compared well to measurements using a cantilever-based mass sensing approach [1,2]. The low stiffness (E_Cu = 130 GPa) can be associated to the carbonaceous matrix material since the Cu content of the deposits was measured to be in the order of 10 at. %.

From the phase relation at resonance the quality factors of the pillars were accurately measured in the order of 100 to 600 at room temperature in vacuum. These values are related to the intrinsic energy dissipation in the material. Multiple (polarized) resonance modes at frequencies related to each other by elliptical pillar cross-sections and pre-bent pillar shapes could be observed by top-view imaging of the vibrating structure (Fig. 3). To our knowledge these are the first systematic dissipation measurements in FEB deposited materials.

References


**Fig. 1:** *In situ* bending test to determine the Young’s modulus via the force-deflection response of the sample pillar. The boxes mark the pillar base and tip position tracked by a cross-correlation image processing algorithm with < 20 nm resolution. Cantilevers were supplied by C. Molhave.

**Fig. 2:** *In situ* modal vibration analysis using the phase-locking technique: Fundamental mode amplitude and phase response of a FEB deposited pillar. Vibrations were induced by piezo-mechanical excitation and detected by the varying secondary electron signal through the interaction of a stationary electron beam with the oscillating structure [3]. The inset shows a wide spectrum of the amplitude response which locates the peak in the vicinity of 566 kHz.

**Fig. 3:** (a) Illustration of the orthogonal polarizations of the vibrations of a FEB deposited pillar. (b) Polarized pillar vibrations have been detected by the secondary electron detection technique as a double amplitude peak and a 90° phase-shift between the two resonances.
Applications of Electron-Beam-Induced Deposition: Additive Repair of Nano-Imprint Lithography Masks and Mechanical Fixation of Carbon Nanotubes

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Electron-beam-induced deposition [1] (EBID) allows the rapid fabrication of three-dimensional nano-devices and metallic wiring of nano-structures within a scanning electron microscope (SEM). The deposited material depends on the precursor chosen; the decomposition of the gaseous precursor is caused by the interaction of an electron beam with a solid substrate. Typical applications of EBID include electrical circuit editing (fig.1), contacting carbon nanotubes [2], and growth of tips for field emission [3] and for magnetic force microscopy [4].

Here we present two applications of EBID. Firstly, we used electron-beam-induced deposition of platinum from methylcyclopentadienyl-platinum-trimethyl (MeCpPtMe3) in a scanning electron microscope (SEM) with a focused electron beam to mechanically fix carbon nanotubes (CNT) to tungsten tips. These devices were intended for testing as an electron emitter. Without the platinum fixation, transport of the devices from one experimental location to another resulted in detachment of the CNT from the tip. With the platinum present, transportation of all devices was successful (fig.2). Previously published literature demonstrated carbon deposition for mechanical fixation [5]; in this study we used platinum to attempt a better electrical connection between the tungsten tip and the CNT. In the normal case, to obtain emission from CNTs on tungsten tips it is required to operate at 700 °C (also, a cleaning “flash” also at 700 °C is required). When emission was attempted from the devices however, after 5 minutes due to the high temperatures the carbon within the deposited material had vaporised and the platinum had migrated down the tungsten tip (fig. 3).

Secondly, we demonstrate additive repair of nano-imprint lithography (NIL) masks using EBID deposition of platinum from methylcyclopentadienyl-platinum-trimethyl (MeCpPtMe3) in an SEM with a focused electron beam onto the master bulk quartz mask. Such work has been reported previously for ion-beam-induced repairs [6] but use of the standard platinum precursor with the electron beam on such substrates has not been extensively documented yet. Optimised parameters were found for deposition on this bulk insulating material (fig. 4); in this case using a 1.6 kV and 40 pA beam (this current was chosen to ensure a sufficient rate of deposition for EBID). Nevertheless problems with drift due to charging and long deposition tails were found. Despite this we show that single lines of width (32 ± 6) nm are easily reached (fig. 5), and that the deposited material withstood the subsequent processing of the NIL mask well.

References

Figures

Fig. 1: Application of EBID to electrical circuit editing: repairing a broken electrode with a simple deposited patch.

Fig. 2: The carbon nanotube is mechanically fixed to the tungsten tip with platinum deposition using EBID.

Fig. 3: After electron emission experiments with the CNT, operating at 700 °C for 5 minutes, it was found that the carbon in the deposited material had vaporized, and that the platinum had migrated down the tungsten tip and clustered into grains.

Fig. 4: Two deposited structures on bulk quartz, next to two Cr lines.

Fig. 5: (left) SEM image and (right) schematic representation of Pt deposits on the bulk quartz mask near a Cr line. Clockwise from top left: a filled star, a vertical pillar, an unfilled star, and two beam parking artifacts. The linewidth of the unfilled star was (32 ± 6) nm.
The Integration of EBIE into a SIMS tool: Towards Quantitative Depth Profiles with High Resolution and a Better Understanding of the Etch Mechanisms

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New material characterization technique based on EBIE

Nowadays, the number of FEBIP applications is increasing drastically. In this contribution, we demonstrate a new material characterization technique which is based on EBIE [1,2]. Due to the scaling of CMOS devices, the surface and interface properties of the semiconductor structures together with an accurate dopant profiling (quantitative depth profiles with a high depth and spatial resolution) will become more important. Due to its high sensitivity and depth resolution, Secondary Ion Mass Spectrometry (SIMS) has still a leading position in compositional analysis. However, the fundamental SIMS physics limits these targets due to the ion-solid interactions (e.g., atomic mixing, matrix effects...) [3].

To overcome these limitations, the ion beam sputtering process will be replaced by an EBIE process which will result in depth profiles with high (near atomic?) depth resolution and spatial resolution. Quantitative identification of the volatile reaction products (partly composed of substrate material) is further based on photo-ionization of the elements by using ultra-short high-power laser pulses and subsequent mass detection. This new approach, called zero-energy SIMS, is schematically shown in Fig. 1.

Initial results with XeF$_2$ as etching gas will be presented. These experiments are performed on a commercial SIMS tool (Cameca IMS 5f) based on a magnetic sector which is adapted for EBIE. As proof of principle, a highly doped boron CVD layer on a silicon substrate is characterized with the zero-energy SIMS technique without laser post-ionization. The obtained results will be compared with state of the art SIMS results based on low energy ion beam sputtering.

Mass spectra and kinetic energy distributions of the EBIE reaction products

The integration of the EBIE process into a SIMS tool can be very useful to get more insight into the etch mechanisms. Until now, the amount of published work on which parameters control the EBIE process is still very limited. To achieve monolayer resolution in zero-energy SIMS, a controlled EBIE process is crucial. The detailed analysis of the volatile EBIE reaction products is a first important step to understand the fundamental etch mechanisms. Until now, only related process like spontaneous etching and ion enhanced etching of Si and/or SiO$_2$ with XeF$_2$ are described in detail [4].

We will present mass spectra of the desorbing species from the EBIE process of Si, SiO$_2$ (see Fig. 2) and Ge with XeF$_2$ as etching gas. These spectra are obtained when a positive voltage was applied to the substrates, hence, only positive ions originating from an electron stimulated desorption (ESD) process or created in the gas phase by electron impact ionization can be detected. Based on the kinetic energy distributions of the volatile species, we can get more insight into the etch mechanisms.

References


Fig. 1: Schematic overview of zero-energy SIMS.

Fig. 2: Mass spectrum of SiO$_2$ EBIE with XeF$_2$ as etching gas.
Electron Stimulated Materials Processing for Nanofabrication and Bio-Inspired Synthesis

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Electron–beam induced processing (EBIP) is a direct–write technique well suited for the deposition and/or etching of nanoscale features [1]. Sub-10 nm spatial resolution [2] has been achieved; resolution limiting factors revealed [3-5] and the statistics of ~1 nm resolution features quantified [6]. The success of EBIP as a nanofabrication process can be traced to several key advantages. The EBIP spatial resolution limit intersects the length scale where many nanoscale phenomena are realized < 20 nm. Moreover, nanoscale and 3D features can be grown at room temperature thus minimizing integration issues. EBIP is fully compatible with ancillary pattern generating soft/hardware used for electron beam lithography on conventional scanning electron microscopes making the process scalable.

Here we discuss the relevant electron–beam induced deposition (EBID) growth parameters that enable the use of EBID to deposit/etch features for specific applications. Accelerating voltage, current, dwell time and precursor refresh times, precursor flux were varied to achieve the optimized condition per application. Results are discussed based on the interplay between emitted electron current density from the nanopillar and precursor gas coverage on and around the nanopillar during EBID. Subsequently, several nanoscale device applications will be demonstrated including, field emission devices, lithography mask repair, scanning probe tip editing, and cellular membrane mimics.

Precise spatial patterning of advanced materials with minimum error is critical for fabrication at reduced length scales where even a single defect can inhibit function. Electron–beam induced processing has emerged as a method to define with high precision nanoscale features and elements. For these reasons, focused beam processing was used to create nanoscale structural elements critical to biomimetic assembly as well as site specific material deposition to enable nanoscale, probe–specific chemical functionalization. These specific techniques provide integral nanoscale, bottom–up fabrication methods that are necessary to complement top–down, microfabrication techniques for the development of multiscale nanobiological and biomimetic [7-9] devices. EBID was used to define nanopillar arrays to serve as the “membrane” mimic component used to regulate the flow of small molecules and nanoparticles into the synthetic cellular interior. EBID also made it possible to both deposit nanoscale gold patterns/features that will be used to support thiol–based chemistries as well as integrated well with standard microfabrication techniques whereby EBID nanopillars were used to physically support a conformal oxide coating to enable silane–based surface functionalization.


Figure 1  EBID deposited nanopillars have been used as the synthetic membrane feature in cell mimic device. The size–selective property of the membranes as well as the transmembrane flux are measured using fluorescence recovery after photobleaching (FRAP) by photobleaching the interior of a nanopillar defined cavity (a,b) and following the recovery of fluorescence by molecular diffusion (c) into this region. The diffusion coefficient of small molecules and nanoparticles can be extracted from the fluorescence recovery data (d). EBID nanopillars (e, left) integrate well with various cell mimic designs including the one shown in (e, right). A narrow and short channel that is roughly the size of a prokaryotic cell is delineated from two microchannel reservoirs by two rows of EBID nanopillars. Upon sealing this connecting channel by a soft, transparent PDMS lid the EBID nanopillar arrays act to regulate fluidic transport into and out-of this region based upon molecule size, diffusion coefficient and nanopillar spacing. We are exploring these structures to regulate biologically relevant reactions.

Figure 2  Vertical growth efficiency and lateral resolution can be increased by, introducing a refresh cycle (τ_r) coupled with a reduction in beam dwell time (τ_d), during each growth loop. These growth parameters are crucial considerations for integrating EBID features with device structures. Above, the increase in final nanopillar height is shown at a function of τ_r and τ_d at constant number of incident electrons. Thus, a taller nanopillar implies a greater EBID efficiency in terms of nm per electron. The efficiency increase will be explained in terms of the interplay between the time and space dependent variables current density and precursor gas coverage.
Fabrication of sub-beam size nanoholes by controlled focused electron beam-induced etching

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1. Introduction

Contrary to focused electron beam-induced deposition (FEBID) [1], the resolution of focused electron beam induced etching (FEBIE) was not yet scientifically assessed. In this work, the control of FEBIE process is examined by fabrication of nanoholes on 10-nm-thin amorphous carbon (a-C) membrane using H2O and XeF2 precursor [2].

2. Experimental procedure

The etching process was carried out in scanning electron microscope (SEM). The a-C membrane was located on a Faraday cup connected to the picoampermeter for time-resolved in situ measurement of the stage current as shown in Fig. 1. Furthermore, Monte Carlo (MC) simulation and knife edge (KE) measurement under H2O flux was also carried out to verify the experimentally obtained results.

3. Results and discussion

The radius of holes is plotted as a function of exposure time in Fig. 2 together with SEM images of the fabricated nanoholes. The etching rate by H2O was about 2.3 times faster than that by XeF2. Each exposure time produced a given nanohole diameter. In the first stage of etching, the nanohole diameter remained zero but the surface of a-C substrate became rough by irradiation. With continuing exposure, nanosized holes were observed and finally, the etching process of the nanoholes reached its saturated diameter given by the low intensity tails of the incident beam distribution.

The part of the incident primary electron distribution traversing through the nanohole will not contribute to secondary electron emission anymore. Current increase during etching process was probably occurred by the change of the secondary electron emission since it had been confirmed by MC simulation that electrons are not back scattered in the 10-nm-thin membrane. Current change is plotted as a function of the radius of the fabricated nanoholes in Fig. 3. Assuming as a good approximation that primary and secondary electrons have the same radial Gaussian distribution, the current change during process can be expressed as a Gaussian function of the radius of the fabricated nanoholes. The Gaussian width and secondary emission yield were varied as a fitting parameter and determined (solid line in Fig. 3). Since MC simulated results for some nanohole geometries agreed well with the analytical fit, edge effects which lead to enhancement of the secondary electron emission seemed to be negligible.

Figure 4 shows the primary electron beam current Ip as a function of the FWHM of the incident beam obtained by etch hole analysis (EHA). Good agreement was found in beam size between EHA and KE measurement with having a theoretically derived power law Ip ∝ FWHM8/3. In contrast, the minimum hole diameters Dmin were not expected to follow this power law since their sizes were controlled by the interruption of exposure according to the time resolved current measurements. The smallest controllable ratio of Dmin to beam size was 0.2. The sub-beam size diameters of our nanoholes can be attributed to the low aspect ratio and the time-resolved in situ control of the process.

4. Conclusion

Sub-beam-size focused electron beam-induced etching of a-C membrane was achieved. The size of the tungsten filament generated electron beam was determined from the in situ stage current monitoring and verified by knife edge measurements. The in situ time resolved stage current measurements as an end point detection allowed the fabrication of nanoholes with a diameter of sub-20 nm, corresponding to 20%-40% of the FWHM of the incident beam.
References


Fig. 1: Experimental setup for the etching process. (Not at scale)

Fig. 2: Radius of holes as a function of exposure (etching) time with a 5 keV and approximately 1 nA electron beam using H₂O (diamonds) or XeF₂ (squares). Insert: SEM images of nanoholes with corresponding exposure time in second.

Fig. 3: Stage current change as a function of radius of nanoholes (primary electron energy = 5 keV and probe current = -924 pA). Analytic and MC models allowed determining the FWHM of the incident beam.

Fig. 4: Beam size (FWHM) as function of probe current obtained by etch hole analysis (EHA) in H₂O. Minimum hole diameters (Dmin) are indicated. Insert: SEM image of 18 nm diameter hole.
Hydrogen microplasma treatment of focused electron beam-induced deposits

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1. Introduction

In spite of attractive advantages for the direct nanofabrication such as high resolution, individual addressing and fast processing rate, focused electron beam induced deposition (FEBID) still has drawbacks. One of them is the formation of the unwanted carbonaceous contamination resulting from the usage of organo metallic precursors [1]. Recently, Botman et al., reported the improvement of the electrical resistivity of the Pt deposits by the ex situ atomic H treatment [2]. On the other hand, our group in Univ. Tokyo developed a low-power and high-flux ultrahigh frequency (UHF; 450 MHz) microplasma source for localized and high-speed materials processing [3]. In this work, we investigated the selective removal of the carbonaceous contamination in FEB Cu deposits by our recently developed microplasma source.

2. Experimental procedure

Micron-size rectangles with a thickness of about 150 nm were fabricated at first by conventional FEBID method using Cu(hfac)₂ precursor in a modified scanning electron microscope (SEM). Then the deposits were irradiated by the atomic and/or ionic hydrogen inside the SEM chamber. Schematics of ex situ hydrogen microplasma treatment is illustrated in Fig. 1. The tip of the plasma torch was located approximately 100 μm from the center of the deposit. For the stable generation argon gas was also induced as a plasma gas. Treatment time, flow rate of hydrogen and bias on substrate were varied as parameter, see Table 1. These microstructures were characterized by field emission-SEM (FE-SEM), energy dispersed x-ray spectroscopy (EDX), and atomic force microscope (AFM).

3. Results and discussion

The fabricated microplasma torch and an example of the generated microplasma are shown in Figs. 2 (a) and (b), respectively. This micoplasma was stably generated with an input power of less than 1.5 W in the chamber pressure range of 10⁻³ and 10⁻¹ Pa, which is suitable for the usage in the SEM chamber [3]. The surface SEM images of the deposit before and after plasma treatment are shown in Figs. 3 (a) and (b). As-deposited surfaces were smooth and flat. The surface became rough and grain structures with sizes of 50-100 nm could be seen after the treatment. The atomic concentration of copper increased and that of carbon decreased with the increase of the flow rate of hydrogen from 0 to 0.21 standard cubic centimeter per minute (sccm). The composition is plotted as a function of the plasma exposure time in Fig. 4. Concentration of copper in the deposit increased more than twice from 62 at.% to 41 at.% and that of carbon remarkably decreased from 11 at.% to 27 at.% with the increase of the treatment time. On the other hand, other elements in the deposit such as oxygen and fluorine did not change (approximately 21 at.% for oxygen and 5 at.% for fluorine). We confirmed that the carbon element in the FEBI deposit was selectively removed from the deposit by the irradiation of hydrogen microplasma.

4. Conclusion

The treatment of FEB Cu deposits was carried out using hydrogen/argon microplasma in the SEM chamber. The surface of the deposit became rough due to selective carbon removal. The concentration of the copper increased by plasma irradiation. This kind of microplasma treatment might be not only useful for the oxygen free removal of carbonaceous contamination but also for the fabrication of other composites such as carbides and nitrides by changing the plasma gas.
References


Table 1: Details of the experimental conditions for microplasma treatment.

<table>
<thead>
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<th>Condition</th>
<th>Values</th>
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<tbody>
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<td>Flow rate of Ar (sccm)</td>
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</tr>
<tr>
<td>Flow rate of H₂ (sccm)</td>
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</tr>
<tr>
<td>UHF power (W)</td>
<td>5 - 13</td>
</tr>
<tr>
<td>Bias on substrate (V)</td>
<td>-30 - +20</td>
</tr>
<tr>
<td>Irradiation time (min)</td>
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</table>

Fig. 1: Schematics of ex situ H₂/Ar microplasma treatment of the FEB Cu deposits from Cu(hfac)₂ (Not at scale).

Fig. 2: Pictures of (a) Fabricated microplasma torch and (b) visualization of generated microplasma at chamber pressure of 10⁻² Pa [3].

Fig. 3: Surface SEM images of (a) before and (b) after 30 min of plasma treatment. (Flow rate of Ar = 0.98 sccm and that of H₂ = 0.21 sccm).

Fig. 4: Atomic concentrations of the deposits plotted as a function of the microplasma irradiated time. (Flow rate of Ar = 0.98 sccm that of H₂ = 0.21 sccm).
Gas Assisted Focused Electron Beam Induced Etching of Carbonaceous Material

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Abstract

Focused electron beam induced processing (etching or deposition) allows localized activation of chemical reactions on the substrate surface with high resolution. Depending on the type of injected precursor, the chemical reactions can induce localized etching or deposition. Localized carbonaceous material removal using electron beam induced etching with water vapor and oxygen has been explored [1,2]. Other assist gases (such as ClF₃ and hydrogen) have also been reported in literature. In this study, the thickness change in PMMA is explored in the presence of electron-beam, residual water in the chamber and Oxygen as the assist gas. Experiments were carried out for various scan parameters (dwell times and replenishment times), beam currents, and impinging oxygen flow rates on the substrate (fig. 1, and 3). Results indicate that oxygen has minimal effect in the efficiency of the process (fig. 2). For all experimental conditions, it was observed that rate of change in PMMA thickness decreased over time. Experimental results indicate that the rate of change (or decrease) in resist thickness (in the dose range of 0.02 to 1200 C.cm⁻²) is independent of the impinging rate of oxygen in the range of 5e13 to 2e17 molecules.cm⁻².s⁻¹, within the chosen experimental conditions. Results also indicate that the rate of change in resist thickness is independent of Replenishment Times and Dwell Times. Rates (in resist thickness change) were similar in continuous irradiation and pulsed irradiation experiments.

Samples coated with structured resist were fabricated. Resist and substrate structuring provided a reference for AFM measurements. The 100 micron large squares were used as test regions (fig. 4). Each square has a unique identifier with small squares allowing rapid identification of test area with various tools such as AFM, XPS, AES and micro-Raman.

Results from this study suggest that the change in resist thickness is significantly dominated by the degassing in resist (in case of PMMA) [3,4,5]. Further experiments are required to be carried out in order to conclude whether oxygen assisted etching contributes to the observed change in resist thickness.

References


Fig. 1: AFM Image of etched holes in PMMA with various etching parameters.

Fig. 2: Etch depths at various dose exposures for different oxygen flows: 5e13, 1e17, and 2e17 molecules cm\(^{-2}\) s\(^{-1}\) (for 0, 1, and 4sccm flows respectively). Current density: 0.05 A cm\(^{-2}\). Residual Water Impinging Rate: 1e14 molecules cm\(^{-2}\) s\(^{-1}\).

Fig. 3: 3D Image of an etched hole in PMMA.

Fig. 4: PMMA and ZEP520A coated silicon and ruthenium substrates were fabricated in clean room.
Scaling Laws for Resolution in Focused Ion and Electron Beam Induced Processing

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Model

Local chemical reactions triggered by focused particle beams involve the physico-chemical processes: molecule adsorption, desorption, diffusion, and dissociation/fixation inside the irradiated area as depicted in fig. 1. The mathematical description of the molecule density \( n \) inside the irradiated area via an adsorption rate equation was set up by Zhdanov [1] and Müller [2]:

\[
\frac{\partial n}{\partial t} = sJ \left( 1 - \frac{n}{n_0} \right) + D \left( \frac{\partial^2 n}{\partial r^2} + \frac{1}{r} \frac{\partial n}{\partial r} \right) - \frac{n}{\tau} \tag{1}
\]

We solved this equation numerically for steady state and an incident Gaussian electron / ion distribution \( f(r) \) [3]. Three important scaling laws which describe the resolution of the process as a function of molecule depletion, diffusion replenishment, and exposure time can be obtained introducing dimensionless variables: a) the molecule residence time ratio:

\[
\tilde{\tau} = \tau_{\text{out}} / \tau_{\text{in}} = 1 + \frac{\sigma f_0}{sJ / n_0} \tag{2}
\]

representing the irradiative depletion of molecules due to dissociation at the centre of the beam; b) the ratio of the diffusion path and the beam size \( FWHM_B \):

\[
\tilde{\rho} = 2 \rho_{\text{in}} / FWHM_B \tag{3}
\]

and c) the ratio of deposit (or etch) size \( FWHMD \) and beam size \( FWHM_B \):

\[
\tilde{\phi} = FWHM_D / FWHM_B \tag{4}
\]

Scaline Laws

The first scaling law of resolution as function of irradiative depletion \( \tilde{\phi}(\tilde{\tau}) \) becomes:

\[
\tilde{\phi} \approx \left( \log_2 (1 + \tilde{\tau}) \right)^{1/2} \tag{5}
\]

The second scaling law of resolution versus diffusive replenishment \( \tilde{\phi}(\tilde{\rho}) \) is:

\[
\tilde{\phi} \approx \left( \log_2 \left( 2 + 1/ \tilde{\rho}^2 \right) \right)^{1/2} \tag{6}
\]

Both scaling laws can be combined in a sort of universal graph in fig. 3, showing the normalized deposit or etch resolution as function of irradiative depletion and diffusive replenishment \( \tilde{\phi}(\tilde{\tau}, \tilde{\rho}) \).

This graph is valid independently of how the normalized parameters are changed, for instance \( \tilde{\tau} \) can be increased by increasing the beam current, \( \tilde{\rho} \) can be increased by reducing the beam size \( FWHM_B \) or by changing precursor diffusion. In combination with deposit shape measurements this approach also allows to deduce ranges for the \( a \ priori \) unknown surface diffusion coefficients and deposition cross sections, see fig. 4.

The third scaling law of resolution as a function of dot exposure (dwell) time \( t_d \) becomes:

\[
\tilde{\phi} = \left( \log_2 (1 + \exp(t_d / \tau_{\text{in}})) \right)^{1/2} \tag{7}
\]

where \( 1/ \tau_{\text{in}} = sJ / n_0 + 1/ \tau + \sigma f_0 \). For typical FEB and FIB cross sections and process parameters a low dose is required to keep the deposit size 10% close to the beam size. Dot exposures in the 30 ns - 0.3 ms range are needed for FEB processing. For FIB processing the range is 1 ns – 0.1 \( \mu s \).
References


Fig. 1: Reference system and processes involved in FEB induced deposition. Inside the irradiated area precursor molecules are depleted by dissociation. Replenishment occurs by gas phase transport and by diffusion. The symbols $J$, $s$, $\tau$, $D$, and $\sigma$ denote the molecule flux, the sticking probability, the residence time, and diffusion coefficient and the dissociation cross section. $V$ is the volume of the decomposed molecule.

Fig. 2: Schematics of incident beam size, size of generated secondary distributions, and deposit size in terms of the full width at half maximum (FWHM). Additionally, the effective residence times $\tau$ and the diffusion paths $\rho$ inside and outside the irradiated area are indicated.

Fig. 3: Normalized deposit size vs. normalized diffusion path for varying irradiative depletion (indicated) [3]. At $\rho = 2$ the diffusion path equals the beam size. Circles represent the second scaling law. The inset shows the FWHM$_D$ definition of indented deposits. Note the three process regimes. The electron limited regime provides the best steady state resolution for the gas-assisted FEB and FIB process.

Fig. 4: Shape fitting with continuum model. AFM image and line scans of FEB deposits from Cu(hfac)$_2$ precursor. Exposure times are indicated. Fits (dashed lines) were obtained with $\sigma = 0.6$ nm$^2$ (= molecule size), $\tau = 10^{-3}$ s (typical value), and $D = 4 \times 10^{-7}$ cm$^2$s$^{-1}$. Other deposition parameters: Gaussian beam with FWHM = 110 nm (5 keV) and $I_0 = 9 \times 10^4$ nm$^{-2}$s$^{-1}$. Precursor supply with $sJ/n_0 = 10$ ML/s [3].
Cantilever-based mass sensor for \textit{in situ} monitoring of gas assisted focused ion and electron beam processes

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Motivation

Deposition and etching with focused ion and electron beams (FIB and FEB) rely on the dissociation of surface adsorbed molecules by incident charged particles and their locally generated energy spectrum. Optimization of gas assisted FIB/FEB processes for reliable fabrication and applications in micro- and nanodevices requires further understanding of the fundamentals: molecule surface kinetics and the deposition and etch efficiency.

Experimental

We showed recently [1,2,3] that an inertial mass sensing method based on micromechanical cantilevers (Fig. 1) allows for femtogram resolution to measure \textit{in situ} and in real-time the deposited/removed mass. The set-up consists of a cantilever with piezo-resistive deflection read-out driven at one of its resonance frequencies by a piezoelectric actuator. Phase-locking of the excitation and response signals is used for continuous frequency and energy dissipation measurements with very high accuracy.

Results

In terms of molecule surface kinetics at the deposition/etching area, the process is a black box in most reported experiments. The cantilever-based mass sensor enables \textit{in situ} monitoring for precursor adsorption and desorption kinetics at the deposition area. Mass loading due to molecule adsorption on the cantilever was measured in the experiment in figure 2 using the precursor $(\mathrm{CH}_3)_3\mathrm{PtCpCH}_3$. The surface coverage at steady-state adsorption-desorption balance was deduced to be around 10\% of the full monolayer coverage.

Furthermore, the FIB deposit density is obtained directly by dividing the measured mass and volume of the deposit generated. In figure 3, a deposit material density of $(11.2 \pm 1.1) \, \text{g cm}^{-3}$ was calculated from the total deposited mass of $(2.8 \pm 0.14) \, \text{pg}$ and the deposited volume of $(0.25 \pm 0.01) \, \mu\text{m}^3$. From the measured density one can finally deduce reliable deposition yields: 1 Pt atom per incident ion (30 keV Ga$^+$). The efficiency of the deposition process and the molecule supply determine the deposition regime which in its term determines the lateral nanometer resolution of the process [4].

Measurements with the mass sensor reveal a change in mass deposition rate with increasing deposition time in FEB induced dot exposures as shown in figure 4. We discuss qualitatively the reasons for this temporal evolution of deposition rate.

References


Fig. 1: Scheme of in-situ inertial mass sensing using a cantilever based sensor for FEB/FIB induced process monitoring. (Precursor supply tube is not at scale.)

Fig. 2: Typical frequency response of the mass sensor during a FIB induced deposition experiment: A) Establishment of precursor adsorption-desorption balance, B) FIB induced deposition and C) precursor desorption (precursor: (CH₃)₃PtCpCH₃).

Fig. 3: Evolution of the FIB (30 kV, 10 pA) induced deposited mass corresponding to part (B) in Fig. 2. Inset: SEM tilt view (52°) of the FIB induced deposit.

Fig. 4: Temporal evolution of mass deposited during FEB (6 keV) induced dot deposition using the precursor Cu(hfac)₂.
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Growth study of silicon nanowires using tungsten wire deposited by FIBID as localized heater.

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We present a method that allows the in situ observation by scanning electron microscope (SEM) of silicon nanowires (Si NWs) growth using Au or Ga as catalyst solvent. In situ SEM nanowire growth offers the ability to “see” events as they occur. To get in situ growth conditions, we induced a localized heating by flowing current through a tungsten submicronic wire made by FIBID. The Vapor-Liquid-Solid (VLS) Si NWs synthesis is obtained by exposing the heated catalyst solvent to an atmosphere of silane [1-4]. For the two different catalyst solvents used (Au and Ga), we have studied the growth mechanism and determined the structure and the composition of the Si NW’s by electron microscopy characterizations.

Experiments were carried out in a nanofabrication station and in a transmission electron microscope (TEM- 2000FX – Jeol) equipped with an energy dispersive x-ray (EDX) analyser. The nanofabrication station is a vacuum chamber containing a cross beam system coupling a scanning electron microscope (SEM - JSM 5910 - Jeol)) and a focused ion beam (FIB – Canion 31+ - Orsay Physics). The nanofabrication station is also equipped with a gas injection system (GIS) and an in-situ electrical module (current-voltage source, picoammeter). For this study, we have developed two original sample devices suitable for in situ SEM localized growth of Si NWs. The first device is based on an Al pattern deposited on a SiO2 substrate using conventional microelectronic processes (Figure 1.a.). The second device is based on four Au electrodes thermally evaporated, through a mask, on a Si3N4 auto supported membrane (Figure 1.b.c.). This membrane is transparent to high energy electrons (thickness 50nm) allowing subsequent analysis in a TEM. Conductive micronic tungsten wires are fabricated on both sample devices between the macroscopic electrodes, by Focused Ion Beam Induced Deposition (FIBID) from organometallic precursor W(CO)6. Structural, chemical and electrical properties of the tungsten wire deposited by FIBID as fully described in previous works [5-6]. The devices can be mounted on the in-situ electrical module allowing the heating of the tungsten wires by Joule effect. The local pressure of silane in the vicinity of the heated wire is obtained using the gas injection system while the base pressure in the chamber is in the 1.5.10^-5 Torr range.

The reaction temperature is a key parameter in the VLS Si NWs synthesis. Based on recent results on nanoscale thermal properties in solid [7-9], we have developed a simulation method to get the temperature profile for different heating conditions of the tungsten wire (Figure 2). The results of temperature simulation can be compared with our experimental results obtained by SEM and TEM observations of Au nanoparticule evaporation. These profiles were useful to estimate the temperature condition for VLS Si NWs synthesis.

We have followed the nucleation and the growth of Si NWs and observed that two very different growth mechanisms are obtained depending on the catalyst solvent (Au or Ga). For Au as solvent (Figure 3-4), the growth mechanism is the classical VLS process, the catalytic droplet is on the top of the Si NW and the growth stops when the temperature of the droplet is below the eutectic temperature. For Ga as solvent (Figure 5-6), only one nanowire grows from its bottom in the vicinity of the gallium droplet, the decomposition of silane is induced by the high temperature of the tungsten wire providing silicon for the VLS synthesis. We have observed that the catalytic droplet remains at the base of the Si NW so that this particular growth mechanism leads to the formation of a unique and very long nanowire.

References:
Figures:

**Figure 1.** SEM images of the SiO$_2$ (a) and Si$_3$N$_4$ (b,c) sample devices

**Figure 2.** SEM images for different heating conditions and the associate temperature profile for a heating at 80µW.

**Figure 3.** Successive SEM images of Si NWs on Si$_3$N$_4$ sample device using Au as catalyst solvent.

**Figure 4.** TEM images of Si NW on Si$_3$N$_4$ sample device.

**Figure 5.** Successive SEM images of Si NW growth on SiO$_2$ sample device using Ga as catalyst solvent.

**Figure 6.** SEM images of Si NWs on SiO$_2$ sample device using Ga as catalyst solvent.