ED NANO 11

10-12 September 2015
Balatonfüred, Hungary

PROGRAMME AND ABSTRACTS

11TH INTERNATIONAL WORKSHOP ON ELECTRODEPOSITED NANOSTRUCTURES (EDNANO-11)

10-12 September 2015
Balatonfüred, Hungary

PROGRAMME
BOOK OF ABSTRACTS

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The workshop is organized by the
Electrodeposited Nanostructures Group
Wigner Research Centre for Physics,
Hungarian Academy of Sciences
Budapest, Hungary

EDNANO-11 Local Organizing Committee

Imre BAKONYI (Chairman), László PÉTER (Secretary),
Katalin NEURÓHR, Bence TÓTH, Sándor ZSURZSA
(Wigner Research Centre for Physics)

History of the EDNANO workshops

EDNANO-1 2001	Budapest, Hungary
EDNANO-2 2002	Budapest, Hungary
EDNANO-3 2004	Newcastle, UK
EDNANO-4 2006	Dresden, Germany
EDNANO-5 2007	Iasi, Romania

EDNANO-6 2008	Berndorf, Austria
EDNANO-7 2010	Bristol, UK
EDNANO-8 2011	Milan, Italy
EDNANO-9 2012	Porto, Portugal
EDNANO-10 2014	Oberwesel am Rhein, Germany

The EDNANO workshop series is supervised by the EDNANO Board established in 2006.

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URL of the EDNANO homepage

www.szfki.hu/ednano

Aims and Objectives

The aim of the EDNANO-11 workshop is to follow the tradition of previous successful meetings in this series of events. It is intended to be a free discussion forum on most recent results on electrodeposited nanostructures and related topics. An important objective is also to provide an opportunity for young researchers to present their results to a community of experienced scientists. The permanently high interest for the EDNANO workshops has ensured also this time that we will have a plethora of interesting presentations of diverse topics. We also have a proper balance of contributions over various research groups representing 34 different laboratories in Europe, 3 in Asia and 3 in America.

Scientific Programme

The backbone of the scientific programme of the EDNANO-11 workshop consists of 34 oral presentations each of 20 min length including a short discussion time. The speakers are marked by underlining in the list of oral contributions which were were assigned to eight consecutive scientific sessions each with 3 to 5 presentations.

A poster session will also be held at the end of the first day of the workshop; currently, we have abstracts for 20 posters and there will be room for a few post-deadline posters as well. The posters will be displayed during both days of the workshop.

According to the policy of the EDNANO event, participants are expected to attend the entire scientific programme. The presenting author of the posters is requested to be present during the poster session and answer the questions of participants.

Venue

The EDNANO-11 workshop will be held in Balatonfüred, Hungary at the Lake Balaton which is a much favoured resort area. Balatonfüred, having a population of 13.000, is the capital of the north-eastern region of the lake and it is easily available from Budapest by public transportation. It is a popular yachting destination as well as a favorite location for fishing. The town has two marinas, a string of carbonated mineral water springs, listed buildings from the middle of the 18th and the 19th centuries. Balatonfüred can offer accommodation for about fifty thousand visitors in the summer and has many fine restaurants. Visitors come to enjoy the mild micro-climate, beautiful scenery, the local wine made of rizling grapes as well as to revive the two-century-old tradition of socializing around spas, bathing and vacationing. The main events of the two-month-long summer holiday season include a ball for first-time visitors with a beauty contest and a wine-tasting festival, both in August. The State Hospital for Cardiology in Balatonfüred boasts the largest cardiac-rehabilitation center in Hungary. The hospital is built on the lake shore and is flanked by the Tagore promenade named after the Nobel-laureate Indian poet Rabindranath Tagore, who was also treated here. Thanks to the carbonated springs and baths, the town was officially declared a spa as early as in 1772.

The venue of the workshop itself will be Hotel Margaréta (http://hotelmargareta.hu/) where the majority of participants will be accomodated. This is a medium-size hotel with an excellent atmosphere for the EDNANO community. It offers a good variety of rooms in two wings, a conference hall, a wellness section including an outside pool and all dining facilities.

Social Programme

In addition to a welcome reception (Wednesday evening) and workhsop banquet (Thursday evening) for all participants, there will be also an optional tour along the Lake Balaton on Saturday.

TECHNICAL PROGRAMME

	WEDNESDAY 9 September 2015
	ARRIVAL
16^{00} – 19^{00}	**REGISTRATION at Hotel Margaréta**
20^{00} – 22^{00}	**Welcome party at Hotel Margaréta**

	THURSDAY 10 September 2015
8^{00} – 8^{45}	**REGISTRATION**
8^{50} – 9^{00}	**OPENING SESSION**
9^{00} – 10^{40}	**SESSION I: Electrodeposited alloys**
	*Chairperson: **Ibro Tabakovic** (University of Minnesota, Minneapolis, USA)*
9^{00} – 9^{20} I-1	**Quartz microbalance studies of iron and iron alloy electrodeposition** V. Haehnel, D. Pohl (Iselt), K. Leistner, Heike SCHLÖRB *Leibniz Institute for Solid State and Materials Research (IFW Dresden), Germany*
9^{20} – 9^{40} I-2	**Studies of additive effects in the anomalous codeposition of Co-Ni alloys** Vinicius Primo GRACIANO[1,2], Walther Schwarzacher[2] [1]*Instituto de Química, Universidade de São Paulo, SP, Brazil* [2]*H.H. Wills Physics Laboratory, University of Bristol, UK*
9^{40} – 10^{00} I-3	**Electrodeposition of Cu-Sn from a choline chloride-based DES** Sudipta ROY[1], Swatilekha Ghosh[2] [1]*Chemical and Process Engineering, Strathclyde University, Glasgow, U.K.* [2]*Material Science, Indian Institute of Science, Bangalore, India*
10^{00} – 10^{20} I-4	**Electrodeposition of nano-scale multilayer structures in the Fe-P system** Timo MÜLLER[1], Andrea Bachmaier[2] and Reinhard Pippan[1] [1]*Erich Schmid Institute of Materials Science, Austrian Acad. Sci., Leoben, Austria* [2]*Chair of Materials Science and Methods, Saarland University, Saarbrücken, Germany*
10^{20} – 10^{40} I-5	**Mictrostructural and composition changes in the near-substrate zone of electrodeposited Fe-Co-Ni alloys** László PÉTER[1], Kristina Žužek-Rožman[2], Sašo Šturm[2] [1]*Wigner Research Centre for Physics, Hungarian Acad. Sci., Budapest, Hungary* [2]*Josef Stefan Institute, Ljubljana, Slovenia*
10^{40} – 11^{10}	**COFFEE BREAK**

$11^{10} – 12^{30}$	**SESSION II: Magnetic nanostructures**
	*Chairperson: **Walther Schwarzacher** (University of Bristol, UK)*
$11^{10} – 11^{30}$ II-1	**Anomalous codeposition of fcc Ni-Fe nanowires with 5-55 %Fe and their morphology, crystal structure and magnetic properties** O. Dragos[1], H. Chiriac[1], N. Lupu[1], M. Grigoras[1], and Ibro TABAKOVIC[1,2] [1]*National Institute of R&D for Technical Physics, Iasi, Romania* [2]*ECE Department, University of Minnesota, Minneapolis, USA*
$11^{30} – 11^{50}$ II-2	**Fabrication of magnetic nanowires via pulse plating methods** Wolfgang E.G. HANSAL[1], G. Sandulache[1], S. Hansal[1], S. Pane Vidal[2] [1]*Happy Plating GmbH, 2700 Wiener Neustadt, Austria* [2]*Institute of Robotics and Intelligent Systems (IRIS), Swiss Federal Institute of Technology (ETH-Zürich) Zurich, Switzerland*
$11^{50} – 12^{10}$ II-3	**Electrodeposition of $Co_{35}Fe_{65}$ nanowire arrays with the highest magnetic saturation, controlled composition and length** Adrian GHEMEŞ[1], H. Chiriac[1], N. Lupu[1], M. Grigoras[1], B. Stadler[2] and I. Tabakovic[1,2] [1]*National Institute of Research and Development for Technical Physics, Iasi, Romania* [2]*Dept. of Electrical and Computer Engineering, Univ. of Minnesota, Minneapolis, USA*
$12^{10} – 12^{30}$ II-4	**Exploiting electrochemistry for voltage controlled magnetic nanostructures** K. Duschek, A. Petr, H. Schlörb, M. Uhlemann, S. Fähler, Karin LEISTNER *Leibniz Institute for Solid State and Materials Research (IFW Dresden), Germany*
$12^{30} – 14^{00}$	**LUNCH**
$14^{00} – 15^{00}$	**SESSION III: Electrodeposited catalysts**
	*Chairperson: **Sudipta Roy** (University of Strathclyde, Glasgow, UK)*
$14^{00} – 14^{20}$ III-1	**Electrodeposition in superimposed high magnetic field – the way to modify catalytic properties of noble metal alloys** Piotr ZABINSKI[1], K. Mech[2], and R. Kowalik[1] [1]*Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals, AGH University of Science and Technology, Krakow, Poland* [2]*Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology, Krakow, Poland*
$14^{20} – 14^{40}$ III-2	**Controlled electrodeposition of Rh-Fe nanoparticles for hydrogen evolution reaction applications** Irati GOLVANO-ESCOBAL[1], Santiago Suriñach[1], Maria Dolors Baró[1], Salvador Pané[2], Jordi Sort[3], Eva Pellicer[1] [1]*Departament de Física, Universitat Autònoma de Barcelona, Bellaterra, Spain* [2]*Institute of Robotics and Intelligent Systems (IRIS), ETH Zürich, Switzerland* [3]*Institució Catalana de Recerca i Estudis Avançats (ICREA), Departament de Física, Universitat Autònoma de Barcelona, Bellaterra, Spain*
$14^{40} – 15^{00}$ III-3	**Controlled design of Pt nanocluster catalysts using different electrodeposition methods** Zakiya AL AMRI, N. Vasiljevic *H.H. Wills Physics Laboratory, University of Bristol, UK*
$15^{00} – 15^{30}$	**Presentation of candidatures for EDNANO-12**

15^{30} – 16^{00}	**COFFEE BREAK**
16^{00} – 17^{00}	**SESSION IV: Microdevice fabrication**
	Chairperson: ***Wolfgang Hansal*** *(Happy Plating GmbH, Wiener Neustadt, Austria)*
16^{00} – 16^{20} IV-1	**Magnetoelectrochemical microdevices** Xiang-Zhong CHEN, Naveen Shamsudhin, Erdem Siringil, Mahmut Selman Sakar, Roel Pieters, Bradley J. Nelson, and Salvador Pané *Multi-Scale Robotics Lab (MSRL), Institute of Robotics & Intelligent Systems (IRIS), ETH Zurich, Switzerland*
16^{20} – 16^{40} IV-2	**Electrochemical Metallization for 3D Printed Microdevices** Roberto BERNASCONI, C. Credi, M. Tironi, M. Levi, L. Magagnin *Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Italy*
16^{40} – 17^{00} IV-3	**Electrodeposited magnets for microfluidic application** Veronika HAEHNEL[1], Xiao Ma[1,2], Christoph Konczak[1,2], Heike Schlörb[1], Annett Gebert[1], Margitta Uhlemann[1] [1]*Leibniz Institute for Solid State and Materials Research (IFW Dresden), Germany* [2]*Faculty of Mechanical Engineering, Technical University of Dresden, , Germany*
17^{00} – 19^{00}	**POSTER SESSION**
20^{00} – 22^{30}	**BANQUET DINNER (Hordó Csárda)**

POSTER SESSION (Thursday, 10 September, 17^{00} – 19^{00})	
P-1	**Solution-based synthesis of Pt-nanoparticle loaded TiO2 nanotubes for catalytic applications** M. Antoni, F. Muench, W. Ensinger *Dept. of Materials and Geosciences, Technical University of Darmstadt, Germany*
P-2	**Electrodeposition of Cd-Ni alloys: comparison of the modified Watts bath and the chloride bath** Krisztina Boros[1], Katalin Neuróhr[1], Lajos Pogány[1], Zsolt E. Horváth[2], Kálmán Vad[3], Attila Csik[3], László Péter[1] [1] *Wigner Research Centre for Physics, Hungarian. Acad. Sci., Budapest, Hungary* [2] *Institute for Technical Physics and Materials Science, Centre for Energy Research, Hungarian Academy of Sciences. Budapest, Hungary* [3] *Institute for Nuclear Research, Hungarian Academy of Sciences. Debrecen, Hungary*
P-3	**This poster was cancelled a few days before the workshop.**
P-4	**Green Electroless Plating of Palladium Nanotubes and their Catalytic Performance in the Synthesis of 4-Aminophenol** E.-M. Felix, M. Antoni, I. Pause, F. Muench, W. Ensinger *Dept. of Materials and Geosciences, Technical University of Darmstadt, Germany*
P-5	**Patterned alumina templates for electrodeposition of diameter-controlled magnetic nanowires** Adrian Ghemes, Oana Dragos-Panzaru, George Stoian, Nicoleta Lupu and Horia Chriac *National Institute of Research and Development for Technical Physics, Iasi, Romania*
P-6	**Magnetic and magnetoresistance studies of electrodeposited Co films and Co/Cu layered structures** S. Zsurzsa, L. Péter, I. Bakonyi *Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary*
P-7	**Electrodeposition of molecularly-engineered conducting polymers for the electroreduction of CO_2** D. Hursán[1,2], B. Olasz[1], G. London[3], C. Janáky[1,2] [1] *MTA-SZTE „Lendület” Photoelectrochemistry Research Group, University of Szeged, Hungary* [2] *Department of Physical Chemistry and Materials Science, University of Szeged, Hungary* [3] *Department of Organic Chemistry, University of Szeged, Hungary*

P-8	**Measurement of Giant Magnetoresistance (GMR) in Ni-Co/Cu Multilayers Prepared by Electrodeposition Method** Marjaneh Jafari Fesharaki[1], Zahra Sadeghi[2], Sohrab Manouchehri[2], Mohammad Hasan Yousefi[2] [1]*Department of Physics, Payame Noor University, Tehran, Iran* [2]*Dept. of Nano Physics, Malekashtar University of Technology, Shahinshahr, Iran*
P-9	**Hydrogen evolution at a platinum microelectrode** F. Karnbach[1], X. Yang[2], K. Eckert[2], A. Gebert[1], J. Eckert[1], M. Uhlemann[1] [1]*Leibniz Institute for Solid State and Materials Research (IFW Dresden), Germany* [2]*Institute of Fluid Mechanics, Technical University of Dresden, Germany*
P-10	**Influence of additives on the microstructure of electrodeposited nanocrystalline nickel** T. Kolonits[1], P. Jenei[2], B.G. Tóth[3], Z. Czigány[1], J. Gubicza[2], L. Péter[3], I. Bakonyi[3] [1]*Institute for Technical Physics and Materials Science, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary* [2]*Department of Materials Physics, Eötvös University, Budapest, Hungary* [3]*Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary*
P-11	**Revisiting the electrodeposition of Fe-Pt alloys** Christoph Konczak[1,2], Xiao Ma[1,2], Karin Leistner[1], Ludwig Schultz[1], Heike Schlörb[1] [1]*Leibniz Institute for Solid State and Materials Research (IFW Dresden), Germany* [2]*Technical University of Dresden, Germany*
P-12	**Texture control and photoelectrochemical water splitting of p-Cu_2O nanowires and nanowire networks via templated electrodeposition** A. Wouter Maijenburg[1], Dominik Dietz[1,2], Liana Movsesyan[1,2], Joachim Brötz[2], M. Eugenia Toimil-Molares[1] [1]*GSI Helmholtzcentre for Heavy Ion Research, Darmstadt, Germany* [2]*Technical University of Darmstadt, Darmstadt, Germany*
P-13	**Biomimetic, self-cleaning metal coatings with superimposed micro- and nanoscale roughness** F. Muench, S. Schaefer, W. Ensinger *Dept. of Materials and Geosciences, Technische Universität Darmstadt, Germany*
P-14	**Electrodeposition of Ni from various non-aqueous media: The case of alcoholic solutions** K. Neuróhr[1], L. Pogány[1], B. G. Tóth[1], Á. Révész[2], I. Bakonyi[1], L. Péter[1] [1]*Wigner Research Centre for Physics, Hungarian Academy of Sciences. Budapest, Hungary* [2]*Department of Materials Physics, Eötvös University, Budapest, Hungary*
P-15	**Adjusting the Fe-Ga deposition to enable nanowire preparation** D. Pohl (Iselt)[1,2], C. Damm[1], D. Pohl[1], L. Schultz[1,2], H. Schlörb[1] [1]*Leibniz Institute for Solid State and Materials Research (IFW Dresden), Germany* [2]*Faculty of Mechanical Engineering, Technical University of Dresden, Germany*

P-16	**Template-based synthesis of Pt-coated magnetic nanostructures and their application as recyclable catalysts for nitrophenol reduction** S. Schaefer, E.-M. Felix, F. Muench and W. Ensinger *Dept of Materials and Geosciences, Technical University of Darmstadt, Germany*
P-17	**Tuning the magnetic properties of multisegmented Ni/Cu electrodeposited nanowires with controllable Ni lenghts** M. Susano, C.T. Sousa, M.P. Proença, S. Moraes and J.P. Araújo *IFIMUP and IN - Institute of Nanoscience and Nanotechnology and Dep. Física e Astronomia, Universidade do Porto, Portugal*
P-18	**Challenges of the electrodeposition of delafossites** A. Varga[1,2], C. Janáky[1,2] [1]*MTA-SZTE „Lendület" Photoelectrochemistry Research Group, University of Szeged, Hungary* [2]*Department of Physical Chemistry and Materials Science, University of Szeged, Hungary*
P-19	**Development of nanowire based structures of bismuth and antimony for thermoelectric applications** M. F. Wagner[1,2,3], F. Vöklein[3], C. Trautmann[1,2], M. Eugenia Toimil-Molares[1] [1] *Materials Research Department, GSI Helmholtz Centre for Heavy Ion Research* [2] *Materials Science Department, Technische Universität Darmstadt* [3] *Institute of Microtechnologies, Hochschule RheinMain*
P-20	**Bimetallic catalysts for ORR and EOR** Claudio Zafferoni[1], Serena Cinotti[1,2], Lok-Kun Tsui[3], Giovanni Zangari[3], Alessandro Lavacchi[4], Massimo Innocenti[1,2] [1]*Department of Chemistry, University of Florence, Sesto Fiorentino, Italy* [2]*INSTM, Research Unit of Florence, Sesto Fiorentino (Florence), Italy* [3]*Dept. of Material Science and Engineering, Univ. of Virginia, Charlottesville, Virginia, USA* [4]*Institute of Chemistry of Organometallic Compounds, ICCOM-CNR, Sesto Fiorentino (Florence), Italy*

FRIDAY 11 September 2015	
9^{00} – 10^{40}	**SESSION V: Semiconductors, thermoelectricity**
	Chairperson: ***Jeremy Mallet*** *(University of Reims Champagne Ardenne, France)*
9^{00} – 9^{20} V-1	**P-type nanowires for micro-thermoelectric devices: synthesis and characterization** Laurent GRAVIER[1], C. Frantz[2], J. Cordelier[1], S. Cho[1], H. Kim[1] and L. Philippe[2] [1]*University of Applied Sciences – Western Switzerland (HEIG-VD/MNT/LAPTE), Yverdon-les-Bains, Switzerland* [2]*Laboratory for Mechanics of Materials and Nanostructures, EMPA, Thun, Switzerland*
9^{20} – 9^{40} V-2	**Diameter dependence of magnetoresistance oscillations in cylindrical bismuth-telluride-selenide nanowires** Svenja BÄSSLER, Bacel Hamdou, Ann-Kathrin Michel, Robert Zierold, Heiko Reith, Johannes Gooth, and Kornelius Nielsch *Institute of Nanostructure and Solid State Physics, University of Hamburg, Germany*
9^{40} – 10^{00} V-3	**(Photo)electrochemical deposition of hybrid semiconductor nano-architectures** G.F. Samu, E. Kecenovity, B. Takács, B. Endrődi, Csaba JANÁKY *Dept. of Physical Chemistry and Materials Science, University of Szeged, Hungary and MTA-SZTE „Lendület" Photoelectrochemistry Res. Group, University of Szeged, Hungary*
10^{00} – 10^{20} V-4	**On the growth mechanism of lead telluride nanostructures** Cédric FRANTZ[1], Charlotte Vichery[1,2], Johann Michler[1], and Laetitia Philippe[1] [1]*Laboratory for Mechanics of Materials and Nanostructures, EMPA, Thun, Switzerland* [2]*Institut de Chimie de Clermont-Ferrand, CNRS, France*
10^{20} – 10^{40} V-5	**Electrodeposition and characterization of p and n sulphide semiconductors** Serena CINOTTI[1,2], Francesco Di Benedetto[3], Andrea Giaccherini[2], Claudio Zafferoni[2], Giordano Montegrossi[4], Annalisa Guerri[2], Francesco Carlà[5], Roberto Felici[5], Massimo Innocenti[1,2] [1]*INSTM, Research Unit of Florence, Sesto Fiorentino, Italy* [2]*Department of Chemistry, University of Florence, Sesto Fiorentino (Florence), Italy* [3]*Dept. Earth Sciences, Universitz of Florence, Italy* [4]*IGG, Istituto di Geoscienze e Georisorse, CNR, Florence, Italy* [5]*ESRF, Grenoble, France*
10^{40} – 11^{10}	**COFFEE BREAK**

11^{10} – 12^{30}	**SESSION VI: Electrodeposition processes and self-organization**
	*Chairperson: **Heike Schlörb** (IFW Dresden, Germany)*
11^{10} – 11^{30} VI-1	**Diamond-like carbon (DLC) thin films produced by electrodeposition** Reinhard BÖCK *Forschungsinstitut für Edelmetalle & Metallchemie (FEM), Schwäbisch Gmünd, Germany*
11^{30} – 11^{50} VI-2	**Green Electroless Plating of Palladium Nanotubes and their Catalytic Performance in the Synthesis of 4-Aminophenol** E.-M. Felix, M. Antoni, I. Pause, F. Muench, W. Ensinger *Dept. of Materials and Geosciences, Technical University of Darmstadt, Germany*
11^{50} – 12^{10} VI-3	**Electrodeposition of indium and indium alloys** Tsvetina DOBROVOLSKA *Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*
12^{10} – 12^{30} VI-4	**Self-organization during electrodeposition of Ag-Sb and Ag-Sn alloys** Aneliya GYOZOVA[1], I. Krastev[2], L. Petkov[1] and T. Dobrovolska[2] [1]*Faculty of Chemical Technology, University of Chemical Technology and Metallurgy, Sofia, Bulgaria* [2]*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*
12^{30} – 14^{00}	**LUNCH**

14^{00} – 15^{40}	**SESSION VII: Metallic nanostructures**
	Chairperson: ***Laurent Gravier*** *(Univ. of Appl. Sciences – Western Switzerland, Yverdon-les-Bains)*
14^{00} – 14^{20} VII-1	**Electrochemical synthesis of highly ordered nanowires with rectangular cross-section using an in-plane nanochannel array** Philip SERGELIUS, Josep M. Montero Moreno, Wehid Rahimi, Martin Waleczek, Robert Zierold, Detlef Görlitz, Kornelius Nielsch *Institute of Nanostructure and Solid-State Physics, Universität Hamburg, Germany*
14^{20} – 14^{40} VII-2	**Electrodeposited Cu-Ni functional materials: microcolumns, nanopillars and nanofoams** Eva PELLICER[1], J. Zhang[1], A. Varea[1], B. Özkale[2], S. Suriñach[1], M. D. Baró[1], S. Pané[2], J. Sort[3] [1]*Departament de Física, Universitat Autònoma de Barcelona, Bellaterra, Spain* [2]*Institute of Robotics and Intelligent Systems (IRIS), ETH Zürich, Switzerland* [3]*Institució Catalana de Recerca i Estudis Avançats (ICREA), Departament de Física, Universitat Autònoma de Barcelona, Bellaterra, Spain*
14^{40} – 15^{00} VII-3	**Electrodeposition of single gold nanocones and multi-cone arrays for field emission** Loïc BURR[1,2], B. Heider[1,2], C. Reimuth[1,2], I. Schubert[1], C. Trautmann[1,2], M.E. Toimil-Molares[1] [1]*GSI Helmholtz Center for Heavy Ion Research GmbH, Darmstadt, Germany* [2]*Technische Universität Darmstadt, Germany*
15^{00} – 15^{20} VII-4	**New synthetic tools for the fabrication of one-dimensional metal nanostructures** Falk MUENCH, M. Antoni, E.-M. Felix, S. Schaefer, W. Ensinger *Dept. of Materials- and Geosciences, Technische Universität Darmstadt, Germany*
15^{20} – 15^{40} VII-5	**Using templated electrodeposition for shaping metal-organic frameworks into one-dimensional nanostructures** A. Wouter MAIJENBURG, Liana Movsesyan, M. Eugenia Toimil-Molares *GSI Helmholtz Centre for Heavy Ion Research, Darmstadt, Germany*
15^{20} – 16^{00}	**COFFEE BREAK**

$16^{00} – 17^{40}$	**SESSION VIII: Non-metallic nanostructures**
	*Chairperson: **Nicoleta Lupu** (Nat. Inst. of R&D for Technical Physics, Iasi, Romania)*
$16^{00} – 16^{20}$ VIII-1	**Highly ordered hexagonal arrays of anodic TiO_2 nanotubes** A. Apolinário[1], P. Quitério[1], C T. Sousa[1], J. Ventura[1], J.B. Sousa[1], J.D. Costa[1], D.C. Leitão[2], J.M. Moreira[1], L. Andrade[3], A.M. Mendes[3] and João Pedro ARAÚJO[1] [1]*IFIMUP and IN - Institute of Nanoscience and Nanotechnology, Dep. de Física e Astronomia, Universidade do Porto, Portugal* [2]*INESC-MN and IN, Lisboa, Portugal* [3]*LEPABE, Dep. Engenharia Química, Universidade do Porto, Portugal*
$16^{20} – 16^{40}$ VIII-2	**Electrodeposition of a-Si nanostructures using room temperature ionic liquids** Shibin THOMAS, J. Mallet*, M. Molinari *Laboratory of Nanoscience, Univ. of Reims Champagne Ardenne (URCA), Reims, France*
$16^{40} – 17^{00}$ VIII-3	**Three-dimensional ZnO nanowire networks fabricated by electrodeposition in etched ion-track membranes as model systems for photoelectrochemical applications** Liana MOVSESYAN[1,2], A. Wouter Maijenburg[1], Noel Goethals[1], Christina Trautmann[1,2], M. Eugenia Toimil-Molares[1] [1]*Materials Research Department, GSI Helmholtz Centre for Heavy Ion Research, Darmstadt, Germany* [2]*Material- und Geowissenschaften, Technische Universität Darmstadt, Germany*
$17^{00} – 17^{20}$ VIII-4	**Supported thick porous anodic alumina membrane on silicon** Bumjin JANG, Reto Siegfried, Xiang-Zhong Chen, Berna Özkale, Bradley J. Nelson, Salvador Pané *Multi-Scale Robotics Lab (MSRL), Institute of Robotics & Intelligent Systems (IRIS), ETH Zurich, Switzerland*
$17^{20} – 17^{40}$ VIII-5	**Influence of thickness and compositional structure on UV-VIS reflectance of anodic aluminum oxide templates** Cristina V. MANZANO[1], J. Best[1], G. Bürki[1], M. Martín-González[2], J. Michler[1], L. Philippe[1] [1]*EMPA, Laboratory for Mechanics of Materials and Nanostructures, Thun, Switzerland* [2]*IMM – Instituto de Microelectrónica de Madrid (CNM-CSIC), Tres Cantos, Madrid, Spain*
$17^{40} – 18^{10}$	**CLOSING SESSION – Announcement of EDNANO-12 venue**

Saturday 12 September 2015	
	EXCURSION
9^{30}	Departure from Hotel Margaréta
17^{45}	Arrival at Hotel Margaréta

10 September 2015

THURSDAY

SESSIONS I-IV

I-1

Quartz microbalance studies of iron and iron alloy electrodeposition

V. Haehnel, D. Pohl (Iselt), K. Leistner, H. Schlörb

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Iron and its alloys can exhibit outstanding magnetic properties, e.g., high coercivity (Fe-Pt), high saturation magnetization (Fe-Co), high magnetostriction (Fe-Ga) or the magnetic shape memory effect (Fe-Pd), making them interesting for a lot of applications ranging from magnetic data storage, sensing and actuating to biomedicine or microfluidics. Depending on the peculiarities of the alloying element, the alloy deposition can be most challenging. Large differences in standard potentials or the tendency of metal ions to hydrolyze are only two of the possible effects that may critically affect the deposition. Therefore, specific electrolyte systems combined with appropriate deposition parameters are required for each alloy system. In order to adjust the alloy composition and microstructure and thus tailoring the magnetic properties for potential applications, a detailed knowledge of the deposition processes and interactions between the electrolyte components is mandatory.

Here we present a study of the iron alloy deposition with Pt, Pd and Ga by means of cyclic voltammetry in combination with electrochemical quartz microbalance experiments. The individual elements as well as binary systems are examined with special focus on the origin and the avoidance of the partially huge incorporation of oxidic species in the deposit. In particular, the interactions of complexing agents with the alloying elements and their impact on the deposition process and the alloy composition and structure will be discussed. The results allow identifying potential routes and appropriate deposition parameters in order to obtain almost oxygen-free, metallic deposits.

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Studies of additive effects in the anomalous codeposition of Co-Ni alloys

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Control over electrodeposition processes, especially those widely used in industry, is highly desirable. Such control can be achieved by the use of additives, such as in the Damascene process. Although control over many deposition processes is available, the mechanism behind some processes remains under debate [1]. The goal in this study is to analyze the effect of additives in alloy deposition in which anomalous codeposition takes place, such as Co-Ni and Zn-Co, using techniques like electrochemical quartz crystal microgravitometry (EQCM) and Fourier transform infrared (FT-IR) spectroscopy.

For Co-Ni baths, glycine (Gly) was used as an additive, while cysteine (Cys) was used for Zn-Co baths for a comparative study. This choice was based on the complexation values between the additives and the metal ions. Data for the variation of film composition with bath concentration showed that Gly decreased the amount of Ni in Co-Ni alloys, making the deposition more anomalous, while Cys decreased the amount of Zn in Zn-Co, making the deposition less anomalous. These results are in agreement with the complexation constants for the additives with the metals.

CVs were measured for the deposition of one metal on top of the other. For Co on Ni, nucleation loops are observed in the absence of Gly, but not in its presence. No nucleation loop is observed for Ni on Co electrodeposition, with or without Gly.

The influence of additives was also studied by EQCM technique. The direct reduction of Co^{2+} is barely influenced by the addition of Gly, while Ni side-reactions are heavily influenced. Unlike in previous work [2], no evidence was observed for hydroxide formation at the surface.

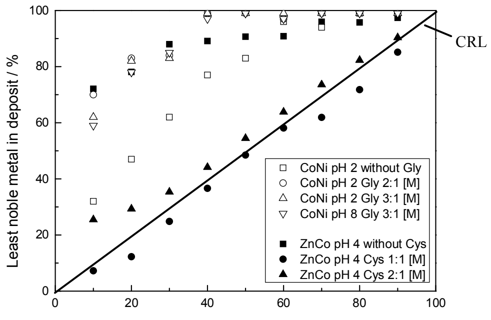

Figure 1. Composition of Co-Ni and Zn-Co films compared to bath composition for different additives and pH values

FT-IR spectroscopy was used to analyze additive adsorption on Ni and Co electrodes. The presence of Gly shifted the limit potential (the potential at which microbubble formation hinders the FT-IR signal) to a more negative value and different forms of Gly (anionic, zwitterionic or cationic) were observed for these electrodes at different pH values.

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Electrodeposition of Cu-Sn from a Choline-Chloride Based DES

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Electrodeposition of metals and alloys from ionic liquids has received considerable attention over the past decade. Despite the huge interest, currently, the most practical ionic liquids which can be used for plating purposes remain deep eutectic solvents (DES). DES are not dry ionic liquids, but are mixtures of compounds which undergo a deep eutectic transition forming an ionic mixture. Here we focus on DES formed by the mixing of choline chloride, (ChCl) and a hydrogen bond donor (ehtylene glycol), called ethaline.

The feasibility of depositing individual metals, Cu and Sn, and the subsequent co-deposition of these two metals have been investigated systematically in this work. Copper and tin have been co-deposited from choline chloride ethylene glycol based DES containing $CuCl_2.2H_2O$ and $SnCl_2.2H_2O$. Initially, electrolyte formulation experiments were carried out containing different amounts of copper and tin at a brass cathode in a rotating cylinder Hull cell. It was found that metallic deposits containing copper and tin could be deposited from a DES containing 0.02 M $CuCl_2.2H_2O$ and 0.1 M $SnCl_2.2H_2O$.

Electrochemical polarisation data has been collected for the individual metals and thereafter, co-deposition of the two components. The effect of DES composition and electrode potential on deposit composition, microstructure and crystallinity has been studied. Anodic stripping voltammetry showed that Sn co-deposits with Cu at -0.36 V, at a lower over-potential than the tin reduction potential. Smooth and bright deposits of thicknesses up to 10 µm were obtained at a potential of -0.36 V or by using a current density of -0.87×10^{-3} Acm^{-2}. XRD analysis showed the formation of mainly Cu_3Sn and some Cu_5Sn_6. Our results suggest that Sn is co-discharged with Cu at potentials which is noble compared to the reduction potential of the individual metal.

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Electrodeposition of nano-scale multilayer structures in the Fe-P system

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Codeposition of iron group elements and phosphorus is regularly applied to obtain amorphous alloys using electrodeposition. It has long been known that the phosphorus content of the deposits depends on the current density and the structure is amorphous beyond a certain amount of phosphorus [1]. Thus, multilayers of different phosphorus content can be obtained by changing the current density periodically during the deposition process.

In this study, Fe-P deposits with periodically changing composition are deposited from a sulphate-chloride bath containing sodium hypophosphite. The composition ranges from the crystalline to the amorphous regime. Special attention is attributed to the transition region where the multilayers contain both a crystalline and an amorphous component (Figure 1).

The structure of the deposits is characterized using electron microscopy and X-ray diffraction techniques. Besides, indentation methods are used to investigate the mechanical properties. Mechanical properties of crystalline-amorphous multilayers are of scientific interest due to the interaction of different deformation mechanisms in the amorphous and crystalline regions. Whereas for sputtered structures investigations on these phenomena have recently been reported in literature [2], the correlation of deposition parameters, structure and mechanical properties in the case of electrodeposits, which is analyzed in this study, has not been investigated yet to the authors' knowledge.

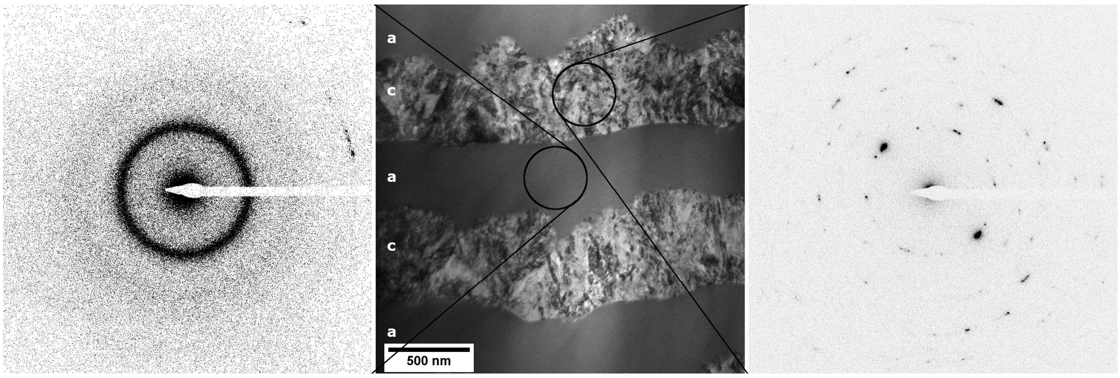

Figure 1. Transmission electron microscopy images of a multilayered Fe-P electrodeposit in the transition region. The bright field image (center) clearly reveals the layered structure with a sublayer width of about 500 nm. The inverted selected area diffraction patterns prove the amorphous (a, left) and crystalline (c, right) sublayer structure.

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Mictrostructural and composition changes in the near-substrate zone of electrodeposited Fe-Co-Ni alloys

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The anomalous codepositon behaviour of the iron-group metals has long been known, leading to the preferred deposition of the less noble metal(s). The spontaneous composition change in the Fe-Ni deposit produced with d.c. plating was described more than half a century ago for Fe-Ni alloys [1]. The composition variation has also been demonstrated recently for ternary Fe-Co-Ni alloys [2,3]. Concerning the microstructure of electrodeposited metals, the general trend is that the non-epitaxial growth on a foreign substrate starts with a nanocrystalline deposit. In weakly inhibited solutions, the initially disordered growth turns into a columnar growth and a pronounced texture may also be produced [4].

In the present study, Fe-Co-Ni alloy samples were deposited from the same additive-free bath with three different current densities. The deposit structure and composition was studied by applying TEM with a Cs-aberration-corrected probe (JEOL JEM-ARM 200CF) at 200 keV. The mapping of the elemental distribution with nanoscale spatial resolution in STEM mode (probe size of 2Å and probe current of 700 pA) was performed by using an EDXS system (JEOL Centurio) attached to the TEM. The goal of the work was to verify the spontaneously occurring composition change in the early phase of the deposition process and compare it with the structural changes found.

The TEM EDX results confirmed that local mole fraction maxima follow each other in the near-substrate region in the order of the deposition preference of the three components. It was also found that composition oscillations occur in the deposit also far from the substrate where a steady-state deposition is achieved. During these composition fluctuations, the mole fraction of Fe and Co changes in a parallel manner, both mole fractions showing an antiphase oscillation with the Ni mole fraction. In this respect, the TEM study fully confirms the earlier depth profile studies [2,3].

All deposits studied show the nanocrystalline to columnar transition along the thickness. Each sample exhibits an fcc structure throughout the deposit, independently of either the crystallite size or the local composition. The variations in the compositional and structural properties appear to be fully independent of each other.

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Anomalous codeposition of *fcc* Ni-Fe nanowires with 5-55% Fe and their morphology, crystal structure and magnetic properties

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The electrodeposition of Ni-Fe nanowires with a length of ~3.0 µm and a diameter of 200 nm into the porous AAO templates was carried out on a sputtered Au-back electrode (300 nm) by using a sulfate/chloride electrolyte solution and pulsed deposition.The electrode area of Au-AOO template, determined by reversible one-electron transfer oxidation of $K_4Fe(CN)_6$, used as a probe in CV, was found to be 2.4 times larger than Au-thin film electrode.

The observed anomalous codeposition phenomena as a „volcano" type curve, with a maximum in Fe-content in Ni-Fe (Fig. 1), was explained earlier [1] by the limited mass transport of Fe^{+2} ions after the peak. This explanation is partially correct, but not complete. The alternative explanation through the surface concentration of H^+ dependent adsorption/desorption of $FeOH^+$ and $NiOH^+$ electroactive species was proposed recently[2].

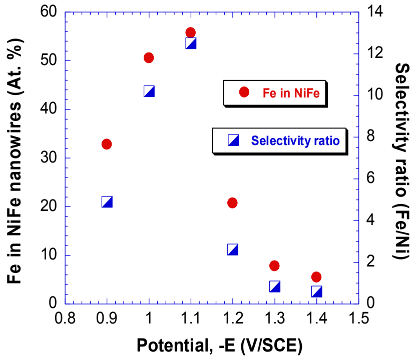

Figure1. Effect of potential on Fe-content in Ni-Fe and selectivity ratio

The distinct decrease of parallel coercivity of Ni-Fe nanowire arrays having the same length was observed with increase of Fe-content in Ni-Fe, which also correlates with the increase of their magnetic saturation. The process of magnetization reversal in Ni-Fe nanowires arrays was investigated, We have found two sets of behavior. In the case of $Ni_{92}Fe_8$ and $Ni_{79}Fe_{21}$ nanowires, coercivity decreases in the 0-90° angular range, which theoretically corresponds to the coherent rotation mode (CR) [3]. In the case of $Ni_{60}Fe_{40}$, $Ni_{56}Fe_{44}$, and $Ni_{45}Fe_{55}$, the coercivity increases, which coresponds presumably to the curling (C) or vortex (V) mode.

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Fabrication of magnetic nanowires via pulse plating methods

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The overall goal of this international project (FP7-ICT-2011-C, MANAQA) is to achieve a technological breakthrough by developing a new method for biological single-molecule measurements. The major technological aim is to develop single-molecule assays by integrating micro-scale cantilevers with magnetic nanowires (NW) electromagnetically controlled along multiple degrees of freedom. For enabling such assays, existing cutting-edge technologies – Atomic Force Microscopy (AFM), nanofabrication, nanowires, and magnetic manipulation – are combined in an integrated approach .

This paper will report on one major part of this project, the electrodeposition of the magnetic nanostructures. Two main lines of magnetic alloys (soft or hard magnetic) were followed, developing the appropriate electrolyte systems as well as the pulse deposition processes. The fundament of these developments has been a comprehensive work package investigating the electrochemical dependencies and reaction mechanisms for controlled alloy deposition. The effect of general plating factors such as pH, alloying metal concentrations in the electrolyte and temperature has been studied.

For the electrodeposition of Co-Ni nanowires, a mixed sulfate-chloride has been used. As substrate, aluminum-coated silicon wafers have been nanostructured using pulse anodising processes. After deposition, the AAO templates were mechanically broken to observe the nanowire growth using back-scatter electron microscopy. The alloy composition of the nanowires were investigated via SEM-EDX. Alternative systems such as Ni-Co-Fe were deposited and compared with the Co-Ni nanowires.

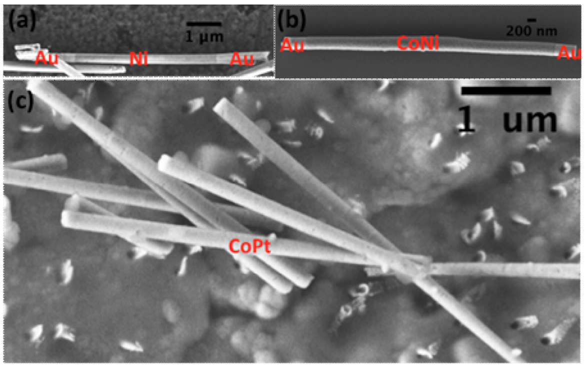

Figure 1. SEM images of Au/Ni/Au, Au/NiCo/Au and CoPt nanowires

The applied pulse sequence allowed the tailoring of the composition of the deposited nanowires. Beside the pulse sequence, the pH of the solution as well as the presence of complex agents (for the alloy formation) were found to be critical parameters for the stability and reproducibility of the alloy deposition process. The deposit properties, e.g. even filling of pores and a homogenous alloy composition along the nanowires were substantially improved by the introduction of pulse-plating techniques. The magnetic properties and their reproducibility were demonstrated with respect to the application targeted.

Electrodeposition of $Co_{35}Fe_{65}$ nanowire arrays with the highest magnetic saturation, controlled composition and length

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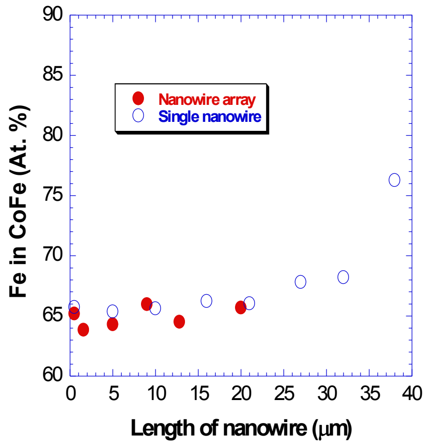
The electrodeposition of $Co_{35}Fe_{65}$ nanowire arrays with varying the length (L= 2-20 μm) and diameters (d= 200 and 35 nm) was carried out using a sulfate/chloride electrolyte solution and pulse electrodeposition. The alloys with $Co_{35}Fe_{65}$ composition having the highest magnetic saturation (2.45 T) are currently used in the industry of modern recording heads as write-pole materials. Most demonstrations in recent years, using nanoparticles and nanowires with high magnetic saturation in treating the cancer tumors, indicate that the higher magnetic saturation brings about the highest possible heating power for magnetic hyperthermia[1].

The length uniformity and composition of the nanowires with d =200 nm and d=35 nm are very well controlled in the range L=2-20 μm. The figure shows the results of composition analysis on nanowire arrays and along a ~40 μm long single nanowire with d =200 nm. In an attempt to obtain nanowire arrays with L=40 μm the nonuniformity in length at L>20 μm and composition was observed. The results of non-uniformity above 20 μm will be discussed in terms of anomalous codeposition.



The XRD patterns showed *bcc* (110), (200), and (211) peaks with the preferred (110) orientation. From the hysteresis curves obtained with the magnetic field applied along the axis direction of the nanowire, the coercivity decreases with the increase of the length of nanowires with d = 200 nm. However, the coercivity increases for nanowires with d = 35 nm. The competition between shape anisotropy and bipolar interactions between nanowires seems to be responsible for the differences in magnetic behavior of the nanowires with different diameters.

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Exploiting electrochemistry for voltage controlled magnetic nanostructures

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Reversible control of magnetism in nano- and microstructures by electric fields is of key interest for novel high density magnetic data storage and multifunctional microsystems like sensors or actuators. At the electrode/electrolyte interface, a multitude of potential dependent electrode processes allow modifying the electrode surface. Accordingly, e.g., the magnetic properties in ultrathin FePt and CoPt films can be tuned in an electrolyte by an external voltage [1,2,3]. Large magnetic changes are obtained when Faradaic processes in the native iron oxide layer on the surface are exploited [2,3]. Such magnetic interface effects based on charge transfer have been named magnetoionic effects recently [4], in contrast to the magnetoelectric effect based on pure electronic changes by e.g. double layer charging [1]. Magnetoionic effects promise larger changes than obtained by magnetoelectric effects since composition, phase and morphology can be affected.

In order to understand and enhance magnetoionic effects, we now lay the focus on reversible electrochemical reactions expected to modify surface magnetism in a controlled manner. As model system, we present oxidation and reduction of an iron/iron oxide layer polarized in 1 M KOH. The electrode reactions were researched by cyclic voltammetry and potentiostatic experiments for bulk and thin film geometry with special regard to reversibility. This allowed determining an upper and lower potential at which dissolution processes are avoided and a maximum effect is attained. The magnetic changes are detected in situ by Anomalous Hall Effect and Ferromagnetic Resonance measurements. A reversible increase and decrease of saturation magnetization of up to 64 % can be achieved for a voltage change of only about 1 V [5]. The combination of such an iron/iron oxide layer as functional top layer exchange coupled to a hard magnetic underlayer such as $L1_0$ FePt or CoPt is demonstrated. This way, also magnetic structures with perpendicular anisotropy can be affected by an external voltage.

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Electrodeposition in superimposed high magnetic field – the way to modify catalytic properties of noble metal alloys

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The properties of cobalt – noble metal alloys for the hydrogen evolution reaction are close to the properties of pure platinum. This makes it possible to use them, for example, in fuel cells. Tests performed so far have demonstrated that for example the Pd-Co alloys are characterized by much better electrocatalytic properties for HER than pure palladium. Application of an external magnetic field during the deposition of an alloy causes an additional convection at the electrode surface through the magnetohydrodynamic effect (MHD), paramagnetic force and magnetic field gradient force. This additional convection results in changes of the alloy composition, structure and morphology, and these, in turn, affect other properties, such as magnetic and catalytic, of the produced alloys.

Magnetic field applied parallel to the surface of the electrode generates convection (MHD effect) of the electrolyte; it results in a laminar flow on the surface of the electrode which reduces the diffusion layer and increases the concentration gradients. This results in change of the size of the grains and thus can also influence the texture and formation of various phases of the deposits. The changes of deposit morphology can be caused also by the magnetic properties of the alloy. When the field is superimposed, the growth of deposit appears in the direction of easier magnetization.

Optimal conditions of the electrolytic deposition of cobalt matrix nanoalloys will be sought through selection of proper composition of electrolyte, changes of electrolysis parameters and by application of external electromagnetic field with intensity up to 12 Tesla. Initial experiments, when the magnetic field was limited up to 1 T, showed the improvement of catalytic properties together with increase of magnetic field orientated parallel to the surface of electrode. The influence of magnetic field with higher strength on electrodeposition of alloys with catalytic properties is needed to be clarified.

Controlled electrodeposition of Rh-Fe nanoparticles for hydrogen evolution reaction applications

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Increasing requests for environmentally friendly processes, as well as for alternative sources to harvest energy are a thrust for the development of materials capable of satisfying both these demands. Hydrogen, an energy carrier with high energy density, is an ideal candidate because it has no deleterious effects on the environment. Hydrogen can be generated by means of several methods such as steam-reforming of hydrocarbons or electrolytic water splitting. The latest is a very attractive approach and it is based on the cathodic reduction of hydrogen, namely, the hydrogen evolution reaction (HER). This reaction can be promoted by electrocatalysts. However, despite tremendous efforts, platinum is still the most efficient electrocatalyst for HER. Therefore, alternative electrocatalytic materials to Pt, and in general to other noble metals (Pt, Pd, Au), are essential to achieve cost-effective electrolytic hydrogen production.

Rhodium (Rh) is a precious transition metal with outstanding catalytic and electrocatalytic properties for HER [1]. Due to its high price, partial replacement of Rh by more abundant and less expensive elements that do not compromise the HER activity is a must. Fe appears as a potential alternative for this purpose [2]. In this work, Rh-Fe based nanoparticles (NPs), with tunable composition (15 at% Fe – 36 at% Fe) and sizes (20 nm – 80 nm) have been electrodeposited onto Au-coated Si substrates at variable current densities and deposition times (Figure 1). X-ray photoelectron spectroscopy analyses show that the NPs exhibit oxidized surfaces and metallic cores. High-resolution transmission electron microscopy observations indicate that the NPs are mostly crystalline. The samples show excellent electrocatalytic activity towards HER in 0.1 M NaOH with a complex dependence on both NP composition and coverage degree. Remarkably, some Rh-Fe samples outperform pure Rh NPs electrodeposited under similar conditions. Moreover, Rh-Fe NPs display reasonably good cycling stability.

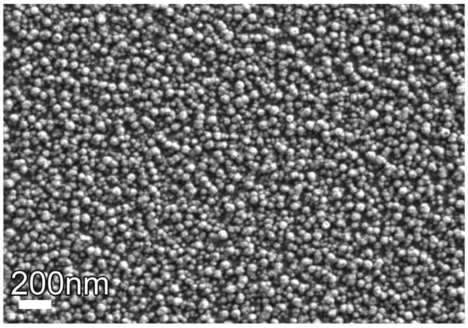

Figure 1. SEM image of Rh-Fe nanoparticles (19 at% Fe) obtained at –0.5 mAcm^{-2} for 1600 s onto Au surface.

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Controlled Design of Pt Nanocluster Catalysts Using Different Electrodeposition Methods

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Design of highly active Pt bimetallic nanostructures has been recently very attractive for the development of commercially viable catalysts for fuel cells applications. Fabrication of Pt nanostructures with the atomic scale control such as the strained monolayers, Pt-alloys and Pt-clusters has been pursued by a variety of methods and on different types of metal systems. The confinement and reduction of the dimensions to few atomic layers coupled with the neighbourhood of Pt to the other metal cause electronic and geometrical effects that can substantially alter the catalytic performance [1-3].

Studies of Pt-nanoclusters have shown strong correlation of surface activity with the structure and distribution of Pt on the catalyst support surface [4, 5]. The modified Au surface with Pt nano-size clusters coverage as low as 15-25% of the substrate area, exhibit very high activity and improved selectivity toward dehydrogenation of formic acid (HCOOH) [4]. Most recently, the formation of Pt monolayer catalysts and nanoclusters using Surface Limited Redox Replacement method has been used to show the effect of strain and morphology [3].

Here in this work we will present a study of Pt clusters electrodeposited on Au using two different electrodeposition protocols to control nanocluster size, and distribution (fractional surface coverage): i) the spontaneous deposition (SD), i.e., the reduction of the spontaneously adsorbed $[PtCl_4]^{2-}$ complex and ii) the surface limited redox replacement (SLRR) method based on the galvanic replacement of Pb and Cu underpotentially deposited layers. The application of the electrodeposition protocol of each method yielded increased Pt surface coverage ranging from 0.25 to 1. The Pt cluster structure and distribution were examined by scanning tunnelling microscopy (STM) and the electrochemical behaviour was analysed by H adsorption, CO stripping and formic electrooxidation. The results show that strength of CO adsorption on SD nanoclusters is weaker than on the Pt films and increases with the increase of Pt surface coverage. For the same Pt nanocluster coverage but with different geometric distribution obtained with two methods CO stripping and selectivity of formic oxidation are altered.

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Magnetoelectrochemical Microdevices

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Recently, there has been a great interest on small-scale localized chemical reactions (LCRs) due to their advantages compared to conventional chemical reaction methods. For example, induced LCRs can provide novel insights to investigate localized chemical and biochemical routes and mechanisms [1,2]. Moreoever, compared to other conventional batch fabrication approaches, LCRs can enable an integrative fabrication of small-scale blocks with different dimensionalities in intricate parts of miniaturized devices. To induce a LCR, several kinds of external stimuli such as heat, electricity, light or combinations thereof can be employed [1,3]. An attractive group of LCRs are localized electrochemical deposition reactions (LECRs) because they combine the advantages of localization together with the versatility of conventional electrodeposition [4]. For example, fine-tuning of material composition and properties can be attained by modulating the applied current density (or potential), or by changing the electrolyte composition. However, electrochemical deposition requires the use of electrodes and electrical connections, which hurdles the implementation of electrodeposited materials in complex micro- and nanomachinery.

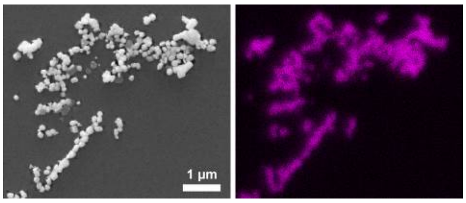

Figure 1. SEM image (left) and corresponding EDX mapping (right) of magneto-electrodeposited gold nanoparticles on a piezoelectric film.

In this work, we report the development of wirelessly controlled magnetoelectrochemical microrobots capable of producing localized electric fields for the deposition of metallic nanoparticles. These microrobots consist of composite hybrid structures containing piezoelectric and magnetostrictive layers. By applying an oscillating magnetic field in the presence of a DC bias field, the magnetostrictive element deforms, thereby transferring a stress on the piezoelectric layer, which in turn becomes electrically polarized. The alternative polarization changes on the piezoelectric surface generate enough electrochemical potential to induce localized electrodeposition of certain metals. Figure 1 shows electrodeposited gold nanoparticles on a piezoelectric film by means of external magnetic fields. Moreover, the magnetostrictive layer renders these devices the ability of being precisely steered by external magnetic fields. These magnetoelectrochemical microrobots offer an innovative way of inducing LECRs with applications in microfluidics, environmental remediation and biotechnology.

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Electrochemical Metallization for 3D Printed Microdevices

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Microelectromechanical systems (MEMS) are nowadays part of everybody's life, since they constitute vital parts of different electronic devices. Important examples include the gyroscopes in smartphones, as well as magnetic and chemical sensors. MEMS manufacturing is dominated by subtractive techniques like lithography applied to silicon wafers [1], which pose significant limitations from the flexibility and process complexity points of view.

A potential way to overcome the disadvantages introduced by these processes is represented by a relatively new technique: 3D printing. It is possible, in particular for small scale productions that require a high customization, to directly 3D print [2] MEMS according to a model elaborated with a CAD or FEA software. This method can thus provide the advantages of an additive technique coupled with a good flexibility and the possibility to adjust in an easy way the production process.

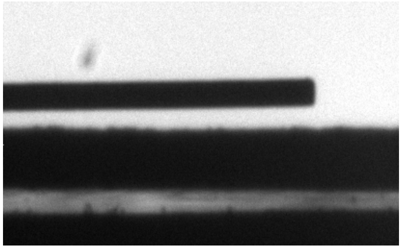

Figure 1. Microimage of the cantilever sensor actuated on a Cu plate. The thickness of the cantilever is 150 µm, while its lenght is 8 mm. A 100 µm air gap is present between the cantilever and the Cu

3D printed microdevices should however be metallized to make possible electrostatic actuation and, most importantly, capacitive reading. It is thus necessary to provide optimized metallization techniques for the polymers used in 3D printing.

The aim of this work is to provide a method for the electroless deposition of NiP alloys and Cu onto photocurable resins used in stereolitography, as this technique is the form of 3D printing most promising for the production of micrometric devices suitable for sensing applications. The foundamental characterization of the deposition process is provided, with the support of appropriate characterization techniques. As an example of the possibilities offered by the additive manufacturing of MEMS, a magnetic sensor produced via stereolitographic printing and metallization is built and actuated (Figure 1). The design selected for the MEMS is cantilever based, making thus possible to use the device also as magnetic actuated microswitch [3]. Sensing performances are estimated in terms of cantilever deflection vs. magnetic field applied and compared with state of the art silicon based devices.

Finally, the possibility of gold plating of the devices is investigated, as nanometric gold layers constitute a good substrate for functionalization and subsequent construction of chemical sensors.

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IV-3

Electrodeposited magnets for microfluidic application

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Microfluidic systems are of immense scientific and technological interest because of their lab-on-chip application potential. Biomedical or environmental analytical approaches as well as mixing, separating or pumping functions are conceivable. Focusing on fluid or particle manipulation in micro- or nanochannels without external mechanical forces, electric, microacoustic and magnetic fields have been proven to alter their flow performance. Most prominent when using homogeneous magnetic fields is the Lorentz force, which acts in electrochemical systems with electric field lines crossing magnetic field lines. It is well known to induce the magnetohydrodynamic (MHD) effect [1]. In this study the rarely investigated method of employing magnetic field gradients [2] is utilized in order to influence fluid motion and separation of magnetic substances in micro- and nanochannels.

We present a concept to design suitable ferromagnetic microstructures and choose applicable materials to generate high magnetic field gradients in the immediate vicinity. Either soft magnetic or permanent magnetic materials of high saturation or remanent magnetization, e.g. Co-Fe or Fe-Pt, respectively, are electrochemically deposited in micro-/nanostructured templates. They are utilized to manipulate paramagnetic ions (e.g. Mn^{2+}) or superparamagnetic particles in microfluidic devices. For this purpose deposition parameters are adjusted to achieve optimized composition and morphology and therefore suitable magnetic properties. Furthermore, to clarify the motion and flow behavior in microchannels in the presence of a magnetic gradient field, first results are supported by modeling the magnetic configuration of the designed microstructures.

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11 September 2015

FRIDAY

SESSIONS V-VIII

FRIDAY
SESSION V

V-1

P-type nanowires for micro-thermoelectric devices: synthesis and characterization

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Electrochemical growth in nanoporous polymer templates provides an easy, cost-effective way to produce nanowire composites for micro-thermoelectric devices. Such applications need both thermoelectric positive (p-type) and negative (n-type) materials. While n-type nanowires are easily synthesized, p-type nanowires are still difficult to obtain.

We present here our results on the synthesis of p-type nanowires, mainly semiconductor compounds like $Bi_{0.5}Sb_{1.5}Te_3$. These structures are characterized via both structural analysis and thermoelectrical energy conversion.

While the Seebeck coefficient and the thermal gradients of $Bi_{0.5}Sb_{1.5}Te_3$ nanowire structures meet our expectations, we struggle to reduce the electrical resistivity to an acceptable level for applications. We finally discuss the comparative advantages/drawbacks of semiconductor vs metallic nanowire structures for thermoelectric applications.

Diameter Dependence of Magnetoresistance Oscillations in Cylindrical Bismuth Telluride Selenide Nanowires

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Cylindrical bismuth telluride selenide nanowires (NWs) with three different diameters (30 nm, 70 nm and 180 nm) are synthesized by electrodeposition in anodic alumina templates with different pore sizes. A millisecond-pulsed electrodeposition method is used to deposit a highly crystalline material. The magnetoresistance (MR) of individual NWs is investigated in a temperature range from 2 K to 300 K for parallel and perpendicular magnetic fields B of up to ±9 T using a lithographically defined contact pattern. High electrical conductivities at zero field (σ = 2900 S/cm for NWs with a diameter of 180 nm and up to σ = 4700 S/cm for NWs with a diameter of 30 nm) are obtained at room temperature, and the conductivity increases with decreasing NW diameter. Moreover, the NWs reveal quantum features in parallel and perpendicular MR at low temperatures. In parallel MR, we observe Aharonov-Bohm oscillations, indicating two-dimensional surface states. In both B-field configurations, weak antilocalization occurs, which may be attributed to the two-dimensional surface or to the three-dimensional bulk states. Additionally observed oscillations in perpendicular magnetic field cannot be explained by two- or three-dimensional states. Instead, our transport analysis indicates that these MR oscillations are the consequence of one-dimensional edge channels at the NW surface that form due to the projection of the external magnetic field on the cylindrically curved surface plane.

(Photo)electrochemical deposition of hybrid semiconductor nanoarchitectures

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Hybrid materials based on conducting polymers (CP) and inorganic semiconductors undoubtedly constitute one of the most promising classes of new materials. The spectacular progress in this research topic has been driven by the development of novel synthetic procedures and by the large variety of applications. In this presentation, it will be demonstrated how to employ (photo)-electrosynthetic methods to obtain such hybrid materials [1]. As it will be shown based on our recent results, both composition and morphology of the hybrid assemblies can be precisely controlled by employing carefully designed electrochemical methods. Hybridization of CPs with metal oxides (TiO_2, WO_3, Cu_2O) [2,3], metal chalcogenides (CdS, CdSe)[4], and carbon nanomaterials (nanotubes, graphene, etc.) [4] will be presented. Beyond scientific and fundamental interest, such hybrid assemblies are attractive from technological perspectives as well, for example, in energy conversion and storage, electronics, catalysis, and optics. In this vein, the most prominent applications of these electrosynthesized materials will also be highlighted.

In the second part of my talk, I will present examples on the use of electrodeposited hybrid semiconductor photocathodes for the photoelectrochemical reduction of CO_2. Given that CO_2 is a greenhouse gas, using sunlight to convert CO_2 to transportation fuel (such as methanol) represents a value-added approach to the simultaneous generation of alternative fuels and environmental remediation of carbon emissions from the continued use of conventional fuels [5]. Photoelectrochemistry has been proven to be a useful avenue for solar water splitting; CO_2-reduction, however, is multi-electron in nature (e.g., 6 e^- to methanol) with considerable kinetic barriers to electron transfer. Due to kinetic constraints, however, it is required to use carefully designed electrode surfaces to accelerate e^- transfer rates to levels that make practical sense in terms of the required energy input. In this talk, particular emphasis will be given on the role of composition and morphology on the photoelectrochemical performance.

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On the growth mechanism of lead telluride nanostructures

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Lead telluride is a low-gap semiconductor used for IR-photodetection and thermoelectric applications [1]. Alternatively, PbTe based compounds are well known for their high thermoelectric figure of merit at high temperatures.

In this work, cyclic voltammetry experiments were conducted for studying the electrochemical behavior of aqueous electrolytes containing HNO_3 (1 M), $HTeO_2^+$, and Pb^{2+} and highlighted a peculiar anodic behavior, later investigated by anodic stripping of electrodeposited PbTe thin films. The diffusion coefficients of Pb^{2+} and $HTeO_2^+$ were determined in order to adjust the electrolyte composition.

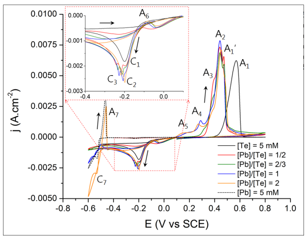

Figure 1. cyclic voltammograms of Au in 1M HNO3 containing $HTeO_2^+$ and Pb^{2+}

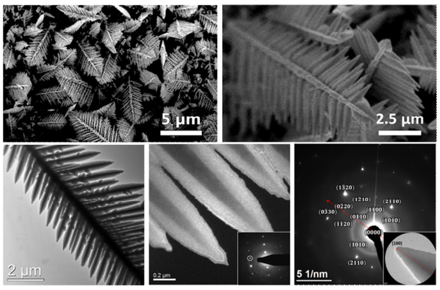

Figure 2. Hierarchical PbTe dendrites grown by potentiostatic deposition

For potentiostatically electrodeposited lead telluride films, the applied potential and the ratio $[Pb^{2+}]/[HTeO_2^+]$ strongly impact on the composition, morphology, and microstructure of the deposits. When the lead content in the electrodeposit is about 50 at.%, prolonged electrodeposition tends to give rise to hierarchical dendrites. The nucleation and growth was studied by electrochemistry and electron microscopy and the formation mechanism of such structures will be discussed.

As shown by the voltamperommetry studies, the presence of dendrites induces an additional anodic peak which was thereby attributed to their selective oxidation. Therefore, reverse pulse potential depositions were considered as a strategy for hindering the dendritic growth. The effect of such deposition technique will be briefly presented [2].

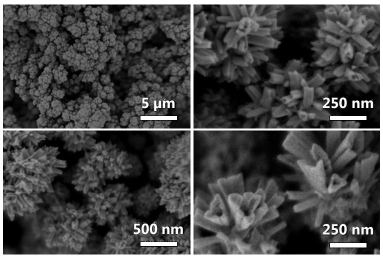

Figure 3. PbTe nanostructured deposits obtained by reverse pulse potential deposition

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Electrodeposition and characterization of p and n sulphide semiconductor

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Semiconductors of interest in the solar energy conversion field were prepared by electrodeposition. In particular, we used the E-ALD (Electrochemical Atomic Layer Deposition) [1] method to build a p-n junction. The obtained ultra thin films were characterised through SXRD (Surface X-Ray Diffraction), with the aim of performing a structural characterization of the grown films.

E-ALD is a layer-by-layer electrodeposition based on the alternate underpotential deposition (UPD) of atomic layers of the elements constituting a compound. The starting point was the deposition of the p layer, (Cu-Zn-S), prepared alternating the UPD of the binary sulfides, CuS and ZnS. After the optimization of the deposition condition of the p film [2-4], the electrochemical behavior of the Cd solution on the substrate covered by the p films has been studied, in order to optimise the deposition of the n film (CdS). To determine the UPD of Cd, voltammetry studies of the Cd solution on the Ag electrode covered by the p films have been done. Under these conditions, the window of electroinactivity of the new substrate is small, thus it is possible to observe the UPD and the bulk reduction peak of Cd, but it is impossible to determine the amount of Cd deposited by linear stripping voltammetric studies, because the redissolution potentials of Cd and Cu-Zn are overlapped . In order to verify the effective deposition of Cd and the UPD nature of the deposition, some different samples have been prepared and then characterized by X-Ray Photoelectron Spectroscopy (XPS) and SEM microscopy and microanalysis. The samples have been growth layer-by-layer, or by EC-ALD, or checking the amount of Cd deposited integrating the charge deposited during time with an appropriate software, in a way to assure the deposition of a single monolayer.

XPS results show the presence of cadmium as sulfide in all the samples and in comparable amount, thus verifying the UPD nature of the cathodic peak at less negative potential.

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Diamond-like carbon (DLC) thin films produced by electrodeposition

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There is a growing interest in diamond-like carbon (DLC) thin film coatings. DLC films exhibit useful chemical and physical properties such as optical transparency, chemical inertness, high hardness or high wear resistance [1].

Recently, the possibility of electrodepositing DLC thin films onto SnO_2 coated glass (ITO glass) or mild steel substrates was demonstrated at low applied voltage ranging between 2-4 V and 8-20 V, respectively [2,3]. In addition to this, a very simple electrodeposition technique was proposed by A.K. Pal et al. [2,4] using formic acid (1-10 v/v) or acetic acid (1-10 v/v) with deionized water as the electrolyte. This approach, employing low potential, low temperature (at or near room-temperature) and simple electrolyte solutions allows, in principle, a notable simplification of the setup and process control.

The aim of a current research project at FEM is to check the process proposed by A.K. Pal et al. for coating of stainless steel substrates with DLC thin films to improve the corrosion resistance and tribological properties of these stainless steel substrates. In this presentation, first results for the electrodeposition of DLC films from electrolytes based on diluted organic acids and deionized water are reported. The effect of applied potential, substrate pre-treatment, acid concentration in the electrolyte, electrolyte temperature and distance of the electrodes on surface morphology and quality of the DLC thin films are demonstrated and discussed.

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Green Electroless Plating of Palladium Nanotubes and their Catalytic Performance in the Synthesis of 4-Aminophenol

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The traditional and well-established synthesis method of electroless plating is a remarkably simple and versatile technique for generating metal nanomaterials. In this technique, often toxic chemicals, such as cyanide as ligands and hydrazine or sodium borohydride as reducing agents, are used [1]. Since environmental and health issues gain much attention, the modernisation of this synthesis method has to be considered now. Based on the *12 Principles of Green Chemistry* [2], we amend the traditional method by exchanging the hazardous chemicals with ascorbic acid and amino acids. The replacements lead to a sustainable plating solution for the synthesis of well-defined palladium nanotubes [3]. The synthesized structures are promising for being used as advanced catalyst in the model reaction of 4-nitrophenol to 4-aminophenol by $NaBH_4$.

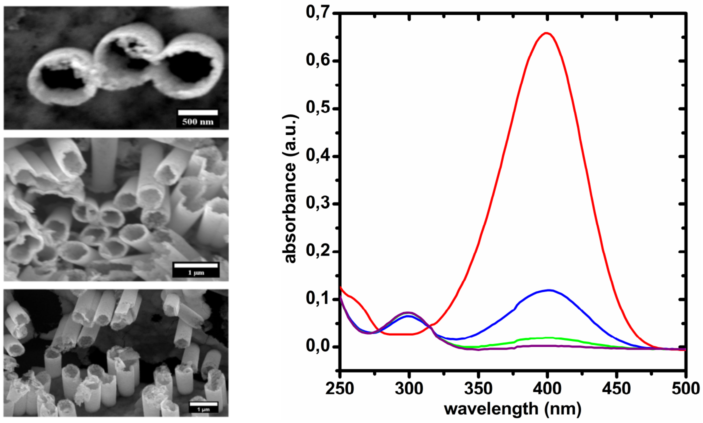

Figure 1: left: Pd nanotubes through a green synthesize route, right: UV-Vis spectrum for the reduction process of 4-nitrophenol by $NaBH_4$. [3]

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Electrodeposition of indium and indium alloys

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An attempt is made to summarize the available information about the electrodeposition of indium and indium alloys. We focus attention on the special features of electroplating from aqueous solutions and its possible perspectives for practical application.

Indium can be electrodeposited from both acidic and alkaline electrolytes. Precipitation of the electrolyte is possible by increasing the pH value above 3.4. In order to prevent the creation of the hard-to-dissolve indium hydroxide under these conditions, ions of ammonia and sucrose (levulose and glucose) are used. Indium alloys have characteristics that depend on specific indium properties such as low melting point, high plasticity, and corrosion resistance.

An improved corrosion resistance compared with nickel is observed in the nickel-indium alloy. The alloys of indium with bismuth, antimony, and tin are used for solders.

The co-deposited indium contributes to a significant decrease of the internal stress of the palladium and ruthenium coatings. Decorative coatings of various colors are obtained by co-depositing indium, palladium, and gold.

A number of separate intermetallic phases of the indium alloys with different metals demonstrate specific properties. For example, shape-memory effects have been registered in the indium-gold, cadmium-indium, and thallium-indium alloys. Intermetallic bismuth-indium compounds are used as zinc anodes in zinc-alkaline batteries; indium-antimonide is a photodetector for infrared and visible rays.

Self-organization phenomena are observed during electrodeposition of several indium alloys. In this case, the increase in the content of the alloying element in electrodeposited alloys reflects the changes of their phase composition when the saturation limit of the lattice of the basic metal is reached. At higher percentages, the excess amount of the alloying element forms one or more new phases richer in this element. The coatings become multi-phase, heterogeneous and their physico-mechanical properties change.

Examples of self-organization phenomena during electrodeposition of different alloy systems could be observed during electrodeposition of indium alloys with Ag, Pd, Co and Ni.

One of the challenges of the electrodeposition of indium alloys is to obtain periodically structured coatings possessing new, unexpected properties, which could increase the possibilities for their application in the micro- and nanodomains.

Self-organization during electrodeposition of Ag-Sb and Ag-Sn alloys

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It is well known, that the silver coatings are widely used in modern technology, due to the properties of this metal - excellent electrical conductivity, high reflectivity, catalytic and antibacterial activity. Alloying silver with small amounts of different metals aims at improving some physical and mechanical properties such as hardness, resistance, resistance to tarnishing and others. A wide variety of spatio-temporal structures are observed during electrodeposition of several silver based alloys, such as Ag–In [1], Ag-Sb [2], Ag-Bi [3]. Some waves can be observed also during electrodeposition of Ag-Sn alloys from cyanide-pyrophosphate electrolytes [4].

From a fundamental point of view, coatings with a sufficient amount of the alloying element are interesting due to fact, that the co-deposition process of two metals could lead to appearance of patterned structures on the surface of the cathode (when the different phases are appeared simultaneously).

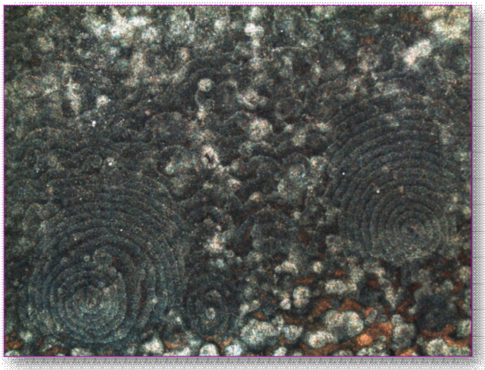

Figure 1. Spiral structures on the surface of electrodeposited Ag-Sn alloy. The coating is obtained from non-cyanide electrolyte.

In both alloys deposition process is of regular type (the silver deposition potential is more positive than that of tin, or antimony) and with increase of the current density the content of tin (or antimony) increases. At tin contents in the deposit of about 45-50 wt. % spatiotemporal structures (waves) can be observed on the electrode surface. The appearance of a wide variety of structures during silver-antimony deposition also could be observed.

In the present study the attempts to develop cyanide-free electrolytes for deposition of a compact silver-tin and silver-antimony coatings in order to investigate their composition, morphology and phase structure are made. As well the idea is to find out the conditions for the appearance and observation of a variety of periodic spatio-temporal structures – figure 1, i.e. phenomena of self-organization in these alloys, deposited from non-cyanide electrolytes.

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Electrochemical Synthesis of Highly Ordered Nanowires with Rectangular Cross-Section Using an In-Plane Nanochannel Array

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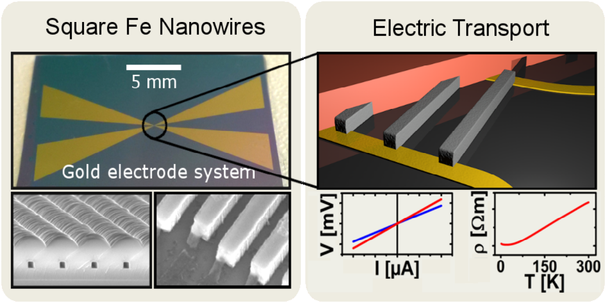
Rapid and reproducible assembly of aligned nanostructures on a wafer-scale is a crucial, yet one of the most challenging tasks in the integration of nanowires into electronic circuits. We present the synthesis of a periodic nanochannel template designed for electrochemical growth of perfectly aligned, rectangular nanowires over large areas. The nanowires can be electrically contacted and characterized in situ using a pre-patterned multi-probe measurement platform. During the measurement, the wires remain within a thick oxide matrix providing protection against breaking and oxidation. We use laser interference lithography, reactive ion etching and atomic layer deposition to create cm-long parallel nanochannels with characteristic dimensions as small as 40 nm. In a showcase study, pulsed electrodeposition of iron is carried out creating rectangular-shaped iron nanowires (70x80x12000 nm^3) within the nanochannels. By design of the device, the grown wires are in contact with an integrated electrode system on both ends directly after the deposition. No further processing steps are required for electrical characterization, minimizing the risk of damage and oxidation. The developed nanowire measurement device allows for multi-probe resistance measurements and can easily be adopted for transistor applications. The guided, in-plane growth of electrodeposited nanowire arrays which are tunable in size and density paves the way for the incorporation of nanowires into a large variety of multifunctional devices.



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Electrodeposited Cu-Ni functional materials: microcolumns, nanopillars and nanofoams

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Electrodeposited copper-nickel (Cu-Ni) alloy films have been extensively investigated for many years owing to their high corrosion resistance, improved malleability and ductility, highly tunable magnetic properties, and excellent electrocatalytic properties [1]. Recently, miniaturization of Cu-Ni building blocks by both template-free and template-assisted approaches has shown to further improve some properties of these alloys and also to provide new ones. In this work, we will review different electrodeposition-based manufacturing strategies for the fabrication of various Cu-Ni architectures, including microcolumns, nanopillars and nanofoams.

First, the growth of high aspect-ratio Cu-Ni microcolumns by localized electrochemical deposition at high overpotentials will be shown [2]. As for continuous films, the addition of saccharine to the bath reduces the porosity of columns and enhances their mechanical properties. Second, the fabrication of periodic arrays of Cu-Ni alloy nanopillars (100 and 200 nm in diameter and 450 nm in length) by means of potentiostatic electrodeposition onto e-beam lithographed Au/Ti/Si(111) substrates will be presented [3]. The composition of alloy nanopillars can be tuned between 34 and 71 at% of Ni by varying the applied potential. The distribution of Cu and Ni elements within the pillars is studied by atom-probe tomography. The coercivity values of the nanopillars are around 100 –150 Oe (in-plane) and 200 – 500 Oe (out-of-plane), as determined by magneto-optical Kerr effect. These values are larger than those for continuous films of similar average composition [1b]. Finally, biphasic Cu-Ni magnetic metallic foams (MMFs) made of Cu-rich and Ni-rich phases are successfully manufactured by electrodeposition taking advantage of hydrogen co-evolution as a source of porosity [4]. The electrochemical activity and stability towards hydrogen evolution reaction of the Cu-Ni MMFs has been investigated by cyclic voltammetry in 1 M KOH at 298 K, and the optimal Ni content is found to be 10 at %.

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Electrodeposition of single gold nanocones and multi-cone arrays for field emission

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High-efficiency cold-field emission cathodes are interesting for applications in flat screen displays or pressure sensors. The fabrication of emitters with nanometer dimensions provides an important reduction of the device size as well as a significant decrease of the turn-on field. The challenge, however, is to develop mechanically stable nanoemitters with high electrical conductivity, and high thermal and chemical stability as required for their reliable implementation into functional devices.

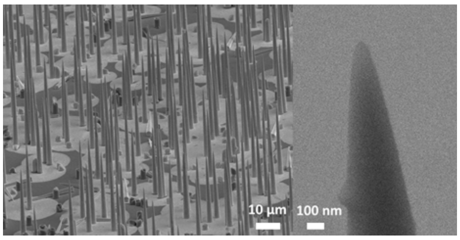

Figure 1. Low-magnification scanning electron microscopy of an array of free-standing gold nanocones (left) and high magnification image of a sharp tip (right)

In this work, we present the fabrication and characterization of gold nanocones free-standing on a solid back electrode. The fabrication consists of several steps. First, polycarbonate templates with asymmetric conical channels (base diameter ~ 2.5 µm, tip diameter ~ 50 nm) are fabricated by heavy ion irradiation and subsequent asymmetric chemical etching of the ion tracks. Second, the nanocones are electrodeposited in the nanochannels starting from the tip to the base to ensure a homogeneous growth and enhance the mechanical stability. After complete filling of the channels, the electrodeposition is pursued on the membrane surface forming a continuous conductive layer (thickness ~ 20 µm) that connects the basis of all cones. Finally, subsequent chemical dissolution of the polymer templates reveals mechanically stable substrates with free-standing gold nanocones. Using this technique, we have fabricated arrays of nanocones with densities between 10^5-10^7 cm^{-2}, as well as single nanocones. The cones adopt the shape of the channels, exhibiting thus a length of 30 µm and sharp tips with diameter down to ~ 50 nm. The field emission properties, such as the maximum emission current, the enhancement factor or the onset field, of the nanowires are being investigated in collaboration with Bergische Universität Wuppertal [1].

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New synthetic tools for the fabrication of one-dimensional metal nanostructures

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In this contribution, we will present some of our efforts to advance existing and develop new processes for the fabrication of anisotropic metal nanomaterials. Three topics will be discussed, each focussing on one specific synthesis aspect:

(i) We illustrate how track-etched polymer templates can be modified to produce novel nano- and microarchitectures. Depending on the pore structure and the deposition mechanism of the applied metallization reaction, new morphologies such as hierarchical wire, tube and tube/wire networks can be prepared (Fig. 1).

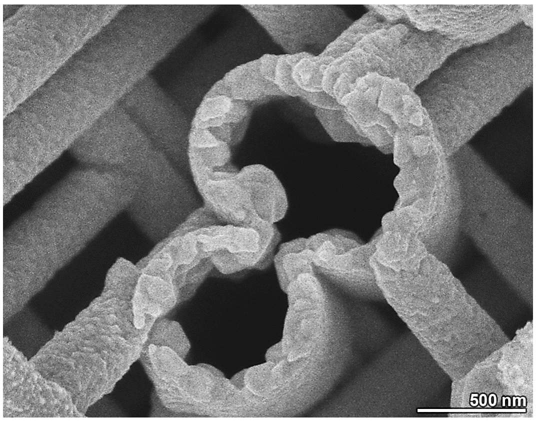

Figure 1. SEM image of a hierarchic assembly consisting of nanostructured Ag tubes and wires.

(ii) We revisit the electroless deposition of Au nanotubes in terms of green chemistry and replace toxic reducing agents and additives with benign chemicals. As an application example, we utilize the nanotubes in the amperometric detection of hydrogen peroxide, and show that their functional properties can be enhanced by introducing porosity to the tube walls [1].

(iii) Inspired by strategies for the synthesis of shape-controlled metal nanoparticles [2], we developed an electroless Au plating reaction which leads to the deposition of Au films consisting of wire-like structures (Fig. 2). The outlined reaction relies only on intrinsic anisotropy induction and does not require hard templates to enforce the one-dimensional structural motif. Thus, it allows the facile synthesis of high-surface-area Au nanomaterials composed of anisotropic building blocks. We demonstrate the possibilities provided by this new class of electroless plating reactions by fabricating a highly efficient electrocatalytic sensor.

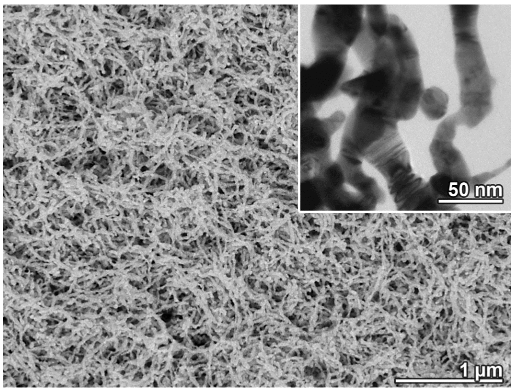

Figure 2. Electron micrographs of Au nanowire films deposited using shape-controlled electroless plating.

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Using templated electrodeposition for shaping metal-organic frameworks into one-dimensional nanostructures

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Metal-organic frameworks (MOFs) are a relatively new class of hybrid materials, which consist of metal ions or clusters as the secondary building unit and organic linkers connecting the metallic building units via coordination bonds of moderate strength [1]. Thereby, MOFs combine the robustness and crystallinity of inorganic materials with the flexibility of organic molecules. Thus, MOFs possess a wide range of unique properties, like framework flexibility, uniform pore sizes, easy functionalization, high porosity and chemical stability [2]. These properties open up the possibility for MOFs to be used in a wide range of applications ranging from gas storage and gas separation to sensors and photocatalysis [1-3].

The synthesis of one-dimensional MOF nanostructures via templated electrodeposition would open up further applications for these MOFs, like photocatalytic water splitting for which a higher absorption of sunlight over the nanowire length combined with efficient charge carrier transport over the nanowire diameter are highly beneficial. Since we use polycarbonate templates fabricated by ion-track technology at the GSI linear accelerator (UNILAC) in Darmstadt, we are able to adjust the geometry (nanowires, nanocones and nanowire networks), diameter (10 nm to a few µm) and length (10-100 µm) of the template in an independent and controlled manner [4]. This provides us with full control over the shape and size of the synthesized MOF nanostructures, depending on the envisioned application. Here, we will present the synthesis of nanowires of the well-known MOF $Cu_3(BTC)_2$ inside-etched ion-track templates by electrodeposition of Cu nanowires and subsequent electrochemical oxidation of these Cu nanowires in the presence of 1,3,5-benzenetricarboxylate (BTC) molecules for the formation of the MOF nanowires (Figure 1).

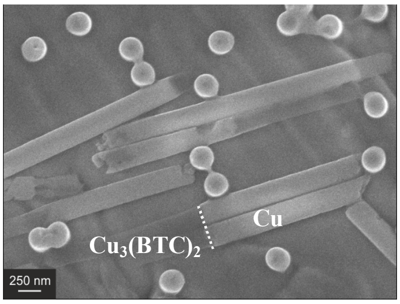

Figure 1. SEM image of $Cu_3(BTC)_2$ MOF nanowires with a diameter of 260 nm after incomplete conversion

Moreover, we are also exploring the flexibility of the presented technique by shaping the same MOFs into nanocones and nanowire networks, and by using different types of ligands for formation of the MOFs. Other ligands can either directly be incorporated during electrochemical oxidation of the Cu nanowires, or via post-synthesis ligand exchange. These results will also be presented during the conference.

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Highly-ordered hexagonal arrays of anodic TiO_2 nanotubes

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Highly-ordered TiO_2 nanotubes (NTs) have gained much importance for application in hydrogen production by water splitting (photoelectrochemical cells) and the dye-sensitized solar cells (DSCs) [1]. The TiO_2 NTs can be synthesized using a titanium foil in fluoride-containing electrolytes via electrochemical anodization method: two-electrode cell with a constant anodization potential in an ethylene glycol solution containing NH4F (0.3 wt%) and H_2O (2 wt%) at room temperature [2,3,4].

It was performed An investigation of the effect of Ti surface roughness on the anodic TiO_2 NTs formation, organization, hexagonal arrangement and length was performed by applying different pre-treatments (chemical etching, electropolishing, mechanical polishing) prior to the anodization,. It was found that pre-treatments that lead to an extremely small Ti surface roughness offer an enhanced NT length and improved template organization quality (highly-hexagonal closed-packed array distribution over larger areas), due to the optimized surface topography [2].

The decisive role played by the electropolishing of the Ti foil on the anodic TiO_2 NTs was unveiled: by tailoring the electropolishing potential (obtaining optimized Ti surfaces with lower roughness and topographic nanopatterning) resulted in longer NT with fast growth rates with higher organization [3].

The role of barrier layer thickness (δ_b) in the bottom of the TiO_2 NTs under different applied potentials and times was analyzed. δ_b grows over time due to the non-steady anodization regime. A relation was established between the phenomenological growth of δ_b with time and applied voltage, $\delta_b(V,t)$, using the high-field Mott and Cabrera conduction theory [4].

Additionally, the general features that govern the porosity and geometrical parameters of self-ordered TiO_2 NTs were studied. A complex cyclic porosity trend was observed in TiO_2 bottoms during constant-voltage anodizations. The self-ordered regime of TiO_2 NTs was found for porosity values in the range of 5.0% to 5.6% [5].

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Electrodeposition of a-Si nanostructures using Room-Temperature Ionic Liquids

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a-Si nanostructures are highly important due to their applications in photovoltaic devices, batteries, biosensors and other semiconductor devices. Even though a number of techniques have been developed for growing silicon nanostructures, most of them involve high temperature, high vacuum, complicated equipments and other rigorous conditions. Moreover, it is difficult to transpose these techniques to future industrial large scale production of the nanostructures.

As an alternative, elemental silicon can be electrodeposited from room-temperature ionic liquids (RTIL) [1]. Template-assisted electrodeposition offers a great control over the size and shape of the Si nanostructures and it allows the growth of nanostructures with varying geometries [2] suitable for various applications.

In order to be a real alternative, the growth mechanism of Si electrodeposition has to be well understood. In the present study, we use Electrochemical Quartz Crystal Microbalance (EQCM) to show the correlation between the viscosity of the electrolyte during the deposition and the morphology of the deposited Si. The influence of various electrochemical growth parameters on the morphology is also discussed. Thanks to this initial studies, Si nanostructures of various geometries were prepared by the template-assisted electrodeposition method.

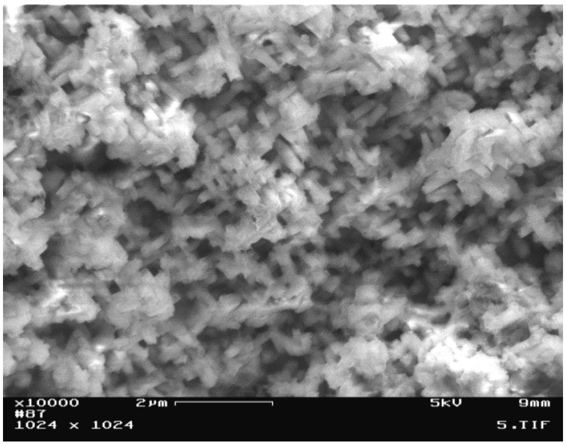

Figure 1: SEM image of interconnecting network of a-Si nanowires deposited from RTIL.

Nanoporous polycarbonate membrane was used for the growth of interconnecting network of a-Si nanowires. Being highly porous, it would be a good electrode for Li-ion batteries and also an interesting material for sensors.

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11th International Workshop on
Electrodeposited Nanostructures (EDNANO-11)
10-12 September 2015, Balatonfüred, Hungary

Three-dimensional ZnO nanowire networks fabricated by electrodeposition in etched ion-track membranes as model systems for photoelectrochemical applications

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Nanostructured photo-electrodes and nanowire-based solar cells are promising due to high absorption of sunlight as well as efficient charge separation and transport [1]. We present the synthesis of three-dimensional (3D) networks of ZnO nanowires. The structures are fabricated by electrochemical deposition of ZnO inside the interconnected pores of polycarbonate membranes produced by ion-track technology at the GSI linear accelerator (UNILAC) in Darmstadt. Heavy-ion irradiation and chemical etching parameters are adjusted to tailor the density, geometry, and diameter of the nanochannels in the membranes [2, 3]. ZnO is used as model semiconductor material to investigate the chemical stability and photoconductivity of nanowire-based arrays compared to their film counterparts.

In order to obtain mechanically stable and self-supporting photoanodes, 3D ZnO nanowire networks were developed by means of optimization of the integration density and wire diameter in the network structure (Figure 1) [4]. The networks were coated with TiO_2 by atomic layer deposition (layer thickness: 4, 10 and 20 nm) to improve their chemical stability during photocurrent measurements in aqueous electrolyte. The photoelectrochemical performance of hierarchical ZnO and ZnO/TiO_2 nanowire networks with diameters varying between 115 and 230 nm and wire densities up to $4\times(2\cdot10^9)$ wires/cm^2 was studied and compared to that of ZnO and ZnO/TiO_2 films. The reduced wire diameter, high surface-to-volume ratio, and the high degree of interconnectivity make these 3D nanowire systems very promising to achieve enhanced efficiency in photoelectrochemical cells due to the larger electrolyte-accessible surface area and the improved transport properties of the photogenerated charge carriers to the photoanode surface.

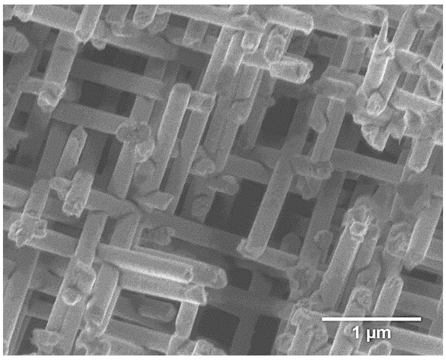

Figure 1. SEM images of ZnO nanowire network consisting of interconnected cylindrical wires with a diameter of 200 nm

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Supported thick porous anodic alumina membrane on silicon

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Porous anodic alumina (AAO) has been widely used for template-assisted electrodeposition to fabricate nanostructures. To this end, two types of AAO templates have been developed: free-standing AAOs and supported AAOs. Free-standing AAO membranes can be obtained by anodization of bulk Al, followed by a wet etching of the remaining Al and the insulating Al_2O_3 barrier layer [1]. To obtain high-aspect-ratio pores with a highly-ordered hexagonal pore arrangement, a two-step anodization is performed. However, the left free-standing AAO membrane is fragile, thus requiring extremely careful handling for further processing. As a conductive substrate is necessary for plating, a metallic layer is usually deposited on one side of the membrane. However, the sealing is not complete. This causes the leakage of the electrolyte during plating and results in a non-uniform deposition. Moreover, free-standing AAO membranes are not suitable as building blocks in micro- and nanosystems due to inherent difficulties in process implementation. On the other hand, supported AAOs (SAAOs) are obtained by anodizing an Al thin film deposited by evaporation on a conductive substrate [2]. Although SAAOs exhibit enhanced mechanical stability compared to free-standing AAOs, the limited thickness of the Al film hinders the feasibility to perform two-step anodization, resulting in low-aspect-ratio pores with a poorly ordered pore arrangement.

To overcome the bottlenecks of the two conventional types, we have developed for the first time a process to integrate thick AAO membranes on silicon (Si) substrates. The process consists of transferring a thick AAO layer onto a Si substrate via a Au/Au compressive bonding process. The function of the sandwiched Au layer is two-fold: (a) it enables the bonding between the AAO membrane and the Si substrate; (b) it serves as a conductive layer for plating. With this method, AAO membranes with high-aspect-ratio pores and ordered hexagonal arrays supported on mechanically robust substrates (Si) are successfully obtained. The remaining barrier layer located at the top part of our SAAO can be easily removed by reactive ion etching (RIE). The anisotropic etching profile provided by the RIE process respects the original pore diameter formed during the two-step anodization. To demonstrate the capabilities of this fabrication approach, Ni nanowires (NWs) were electrodeposited in SAAO membranes. The obtained Ni NWs show both uniform diameter and length of 50 nm and 5 μm respectively. After etching the AAO membranes, Ni NW arrays were standing on the Si substrate. The results show that the process can be successfully employed for the integration of functionalized membranes or ordered NW arrays in micro- and nanosystems.

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Influence of thickness and compositional structure on UV-VIS Reflectance of Anodic Aluminum Oxide templates

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Anodic Aluminum Oxide (AAO) templates have attracted great attention due to many potential applications as in nanotechnology and industry. Self-ordered AAO templates present hexagonal patterning with control over pore diameter, length, interpore distance, and pore density. AAO can be grown by two different processes, a non-lithographic and a two-step anodization. A two-step anodization process allows tailoring the final thickness (from nm to hundrends of microns), diameter (12 nm-400 nm [1-3]), and pore density over macroscopic areas. These templates above anAl substrate could produce a bright colour on reflexion in the visible range due to the light interference.

Ordered anodic aluminum oxide (AAO) templates have been fabricated using a non-lithographic approach, a two-step anodization process in phosphoric, oxalic, and sulphuric acid in order to obtain different pore diameters and interpore distances. The pore diameter of AAO templates was around 400, 140, 50, 30, 20, and 15 nm. The thickness of these templates was 2, 10, 20, and 70 µm.

UV-VIS reflectance spectra of AAO with different pore diameters and thickness were analyzed in order to study the bright colour on reflexion in the visible range. The reflectance is minimum when the thickness of AAO is maximum and a red shift is observed in this case. The reflectance does not depend on the pore diameter as shown in Figure 1.

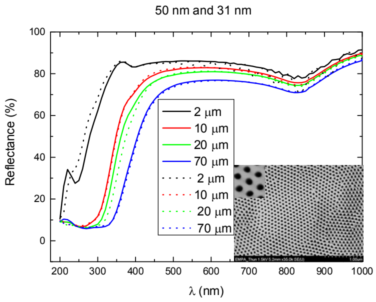

Figure 1. Reflectance as a function of the thickness and pore diameter of AAO.

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10 September 2015

THURSDAY

POSTER SESSION

P-1

Solution-based synthesis of Pt-nanoparticle loaded TiO_2 nanotubes for catalytic applications

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Since the consumption of fossil fuels has reached peak oil status, science and economy have a large interest in alternative drive concepts such as electromobility [1]. Those conceptual designs request new energy sources and storages independent from fossil fuels. One possible and meanwhile well-established energy source for electromobile units is the fuel cell technology. In a fuel cell, the chemical energy of a fuel is converted into electric energy via a chemical reaction with oxygen or an oxidising agent. For instance, ethanol is used within the direct-ethanol fuel cell (DEFC). In comparison to common fossil combustibles, ethanol can be extracted from renewable resources [2]. The necessary oxidation within the fuel cell requires a catalyst, which is often precious metal nanoparticles (NPs) carried on carbon black. Catalyst layers prepared from such materials tend to be disordered and relatively compact. This structure limits mass transport and reduces the accessible catalyst surface area by clogging. Furthermore, carbon is susceptible towards electrochemical corrosion, reducing the long-term stability of classic supported NP catalysts.

To avoid these problems, we developed a route to synthesise nanotube-supported catalysts. These materials are based on TiO_2 nanotubes (NTs) with a large surface to volume ratio, whose outer surface is covered with Pt nanoparticles in a well-defined manner. Aside from benefits resulting from the well-defined structure, the use of TiO_2-supported catalysts is interesting as synergetic effects between Pt and TiO_2 have been observed in previous studies [3].

The starting point for this innovative catalyst system is the use of ion track-etched membranes, which are loaded with Pt NPs using the reduction of $[PtCl_4]^{2-}$ by dimethylaminoborane in the so-called swelling activation [4]. Afterwards, a thin layer of TiO_2 is deposited using a novel precipitation reaction route, resulting in the formation of a nanotube shell to which the Pt NPs are attached. Both synthesis parts are well-controllable, only require simple, solution-based chemical reactions and are suitable for the preparation of various tube diameters and lengths. Furthermore, different metal NP types can be employed. The outlined method thus provides access to a variety of hybrid nanotube materials, which are promising for application in, e.g., energy conversion, photocatalysis, heterogeneous catalysis and sensing.

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Electrodeposition of Cd-Ni alloys: comparison of the modified Watts bath and the chloride bath

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Both nickel and cadmium are prominent components of anticorrosive coatings. They form two equilibrium alloys, Cd_5Ni and CdNi with a few atomic percent homogeneity range [1]. The establishment of the phase diagram of the Cd-Ni system was based on structural studies of metallurgically processed samples [2-4]. Although some studies have revealed the possibility of the formation of these alloys by electroplating [5,6] and their dissolution behaviour [6], no simultaneous electrochemical and structural study is available on the Cd-Ni system. The goal of the present research is to correlate electrochemical, composition and structural properties of Cd-Ni deposits obtained from two bath types, a modified Watts bath and a full-chloride bath.

The solutions were first investigated with cyclic voltammetry. An unusually large difference was found between the voltammograms recorded for macroscopic electrodes and microelectrodes. While at macroelectrodes the Cd deposition and dissolution could hide the signs of alloy formation, the stripping peaks characteristic of the Cd-Ni alloys were always present if microelectrodes were used. This clearly indicates the role of spatial confinement on the codeposition phenomenon. The formation of Cd-Ni alloys could be verified with voltammograms of multiple stages in combination with a quartz crystal microbalance observation.

The ratio of the stripping peaks related to the dissolution of Cd-Ni alloys was different in the two baths. The chloride bath was much more favourable for the alloy formation than the modified Watts bath. If saccharine was also present in the Watts-type bath, the sulphur incorporation to the Cd-Ni alloys was significant, which was identified as a possible reason for the lack of lines corresponding to the alloys in the X-ray diffractograms. However, a few lines of the CdNi phase could be observed on samples produced from the sulphur-free chloride bath. The Ni content of the samples deposited from the chloride bath was much larger compared to the modified Watts bath. The scanning electron micrographs could help to identify the crystals of pure Ni in the deposit.

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P-3

This poster was cancelled a few days before the workshop.

Green Electroless Plating of Palladium Nanotubes and their Catalytic Performance in the Synthesis of 4-Aminophenol

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The traditional and well-established synthesis method of electroless plating is a remarkably simple and versatile technique for generating metal nanomaterials. In this technique, often toxic chemicals, such as cyanide as ligands and hydrazine or sodium borohydride as reducing agents, are used [1]. Since environmental and health issues gain much attention, the modernisation of this synthesis method has to be considered now. Based on the *12 Principles of Green Chemistry* [2], we amend the traditional method by exchanging the hazardous chemicals with ascorbic acid and amino acids. The replacements lead to a sustainable plating solution for the synthesis of well-defined palladium nanotubes [3]. The synthesized structures are promising for being used as advanced catalyst in the model reaction of 4-nitrophenol to 4-aminophenol by $NaBH_4$.

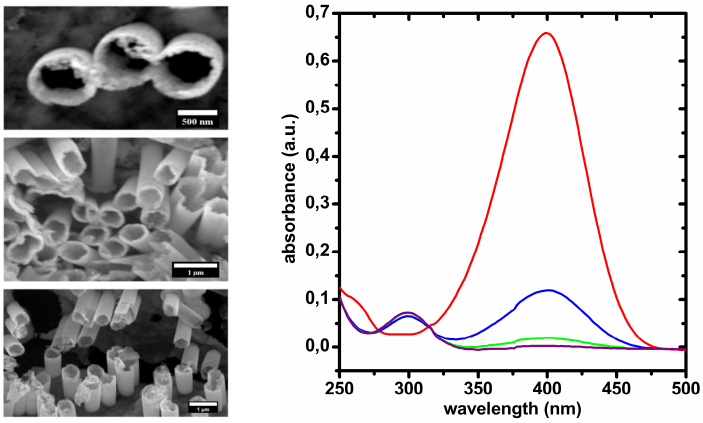

Figure 1: left: Pd nanotubes through a green synthesize route, right: UV-Vis spectrum for the reduction process of 4-nitrophenol by $NaBH_4$. [3]

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P-5

Patterned alumina templates for the electrodeposition of diameter-controlled magnetic nanowires

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Recently, magnetic nanowires have been increasingly studied, their small size and unique properties making them attractive to be used in a variety of application areas like electronics, recording media or sensing applications. Many research groups were using hexagonally arranged nanoporous alumina membranes in order to obtain arrays of magnetic nanowires with the same diameter over the entire area of the substrate [1, 2]. For sensing applications, a small change in the magnetization state of these nanowires can be detected and transformed into an electrical signal as shown in Figure 1a.

Our reasearch aims to obtain, onto the same alumina membrane, areas with different and controlled diameters of the nanopores. When nanowires are deposited into such a structure, we will be able to detect separate signals from each area and these signals will be proportional to the diamater of the nanowires (see Figure 1b).

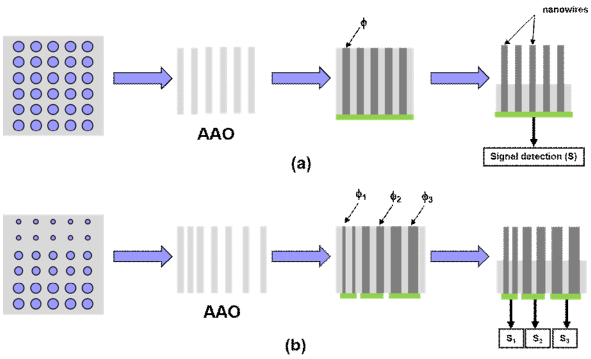

Figure 1: (a) Commonly used alumina template and (b) Proposed structure

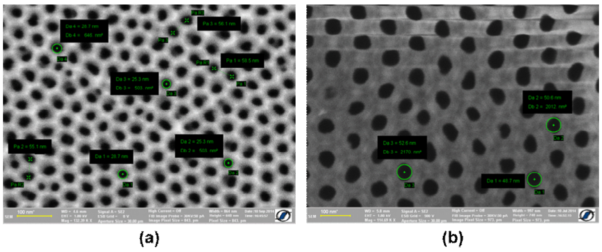

Figure 2: Hexagonally arranged nanopores obtained in (a) H_2SO_4 and (b) $H_2C_2O_4$

To obtain the desired structure, we used the two-step anodic oxidation [3] of pure Al sheets in acidic electrolytes. By successive anodization processes, we obtained two regions with nanopores of 25 nm in sulfuric acid at 40 V and 17 °C and 50 nm in oxalic acid at 22 V and 3 °C as we can see in Figure 2. Attempts to obtain larger diameter nanopores in phosphoric acid failed due the strong etching effect of this acid on the formed alumina layer. We are working now on creating a non-porous, barrier-like alumina layer between the defined porous regions and eliminating the remaining aluminum in order to obtain a free-standing structure for nanowire electrodeposition. These results will be presented at the meeting.

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Magnetic and magnetoresistance studies of nanometric electrodeposited Co films and Co/Cu layered structures

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With the aim of achieving a spin-valve structure containing ferromagnetic layers with different coercivities which are separated by a non-magnetic spacer layer, first we studied the effect of magnetic layer thickness on the magnetic and magnetotransport properties of nanometric electrodeposited Co films with a protective Cu layer and Co/Cu layered structures.

The samples were electrodeposited from a sulphate bath on a [100]-oriented, 0.26 mm thick Si wafer covered with a 5 nm Cr and a 20 nm Cu layer by evaporation. The purpose of the chromium layer was to ensure adhesion and the Cu layer was used to provide an appropriate electrical conductivity for the cathode surface. The magnetization and magnetoresistance curves (M(H) and (MR(H), respectively) were measured at room temperature in magnetic fields up to H = 8 kOe. The coercive field H_c and the peak position H_p of the MR(H) curves were investigated as a function of the magnetic layer thickness d_{Co} for various layered structures.

The single Co films exhibited anisotropic magnetoresistance (AMR), whereas the layered structures Co/Cu/Co/Cu and Co/Cu/Co/Cu/Co/Cu as well as the Co/Cu multilayers (all with a constant Cu layer thickness of 5 nm) exhibited giant magnetoresistance (GMR) up to about d_{Co} = 15 nm. Beyond this Co layer thickness, AMR was observed also in the layered structures.

According to Figure 1, H_p reduces from about 100 Oe to 20 Oe as the Co layer thickness increases to 20 nm. Although the data show some scatter, it can be observed that for a given Co layer thickness, H_p is roughly the same for the single Co films and for the various Co/Cu layered structures. Since H_p is a measure of coercivity, the common H_p values may hint at the absence of a coupling between the magnetic layers in the Co/Cu layered structures.

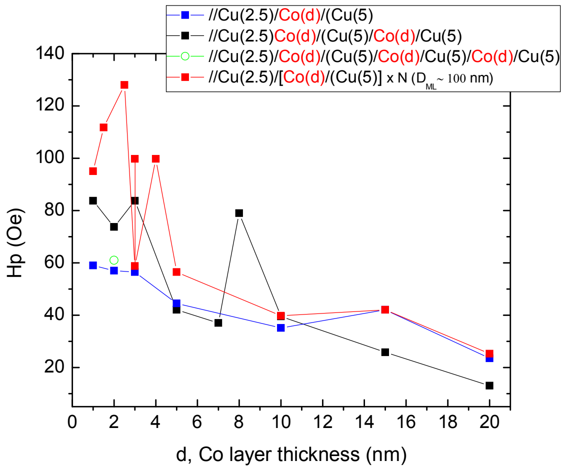

Figure 1. H_p variation with Co layer thickness for Co films (blue) and for various Co/Cu layered structures: black: Co/Cu/Co/Cu, green: Co/Cu/Co/Cu/Co/Cu, red: [Co/Cu] x N (D_{ML} ~ 100 nm)

Electrodeposition of molecularly-engineered conducting polymers for the electroreduction of CO_2

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The drastic increase in the atmospheric CO_2 concentration in the last three decades and the global warming associated with it has drawn attention to the search for efficient CO_2 reduction technologies. Electrochemical and photoelectrochemical processes are among the most promising possibilities. To exploit the above strategies, carefully designed catalyst materials are required. Conducting polymers are viable candidates in this manner [1].

In this work, we present electrosynthetized conducting polymers with improved adsorption and catalytic properties. Two basic approaches are presented: i) synthesis of polymers with regulated adsorption and catalytic sites (design of new monomers) ii) synthesis of conducting polymer (composite) nanostructures in order to improve electron-hole separation and/or CO_2 adsorption.

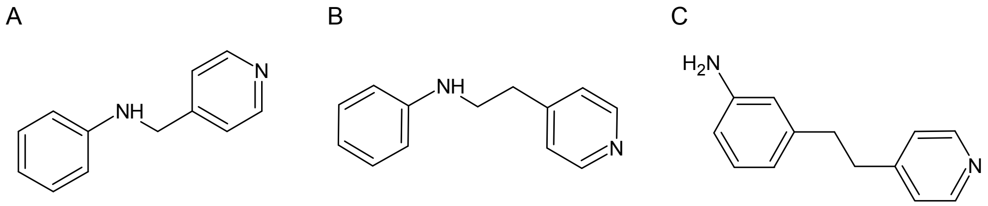

Fig.1.: Structure of the newly-designed monomers.

For the first, one polyaniline-based materials with pyridine substituents (which is an electrocatalyst of the electrochemical CO_2) were electrosynthetized. For the second, nanoporous phytic-acid-doped polyaniline and polyaniline/CNT composites are prepared. The electrochemical behavior and adsorption properties of the polymers and composites are presented with the aim that later these materials can be used in (photo)electrochemical CO_2 reduction.

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P-8

Measurement of Giant Magnetoresistance (GMR) in Ni-Co/Cu Multilayers Prepared by Electrodeposition Method

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In this research, Ni-Co/Cu multilayers were first prepared by electrodeposition method under potentiostatic condition. Then magnetoresistance (MR) characteristics of multilayers were investigated at room temperature as a function of the ferromagnetic (Ni-Co) and nonmagnetic (Cu) layer thickness. The maximum giant magnetoresistance (GMR) value was obtained for a Ni-Co/Cu multilayer with $d_{Ni\text{-}Co}$(4nm)/d_{Cu}(4nm) thickness as shown in Figure 1.

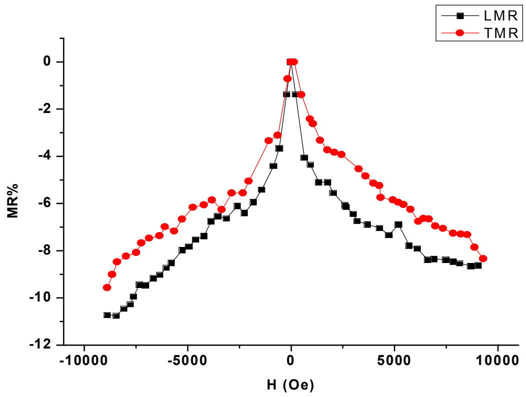

Figure 1. LMR and TMR magnetoresistance for ED Ni-Co/Cu Multilayers

The temperature dependence of the magnetization for the $d_{Ni\text{-}Co}$(3nm)/d_{Cu}(3nm) and $d_{Ni\text{-}Co}$(4nm)/d_{Cu}(2nm) multilayers were investigated by Faraday balance as shown in Figure 2. The decrease of the magnetization with the increase of temperature will be discussed according to electron scattering due to spin fluctuations [1].

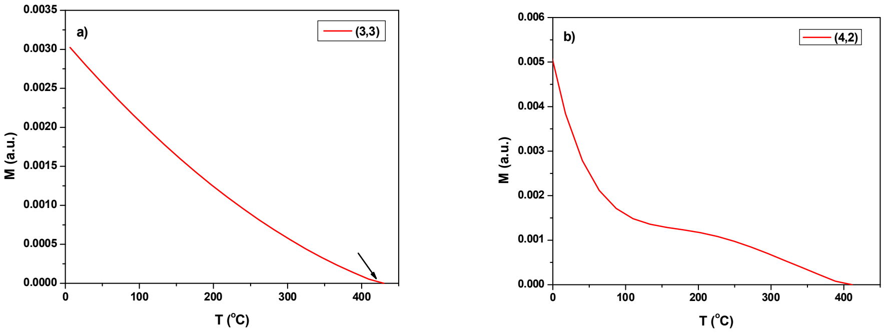

Figure 2. The temperature dependence of the magnetization for ED Ni-Co/Cu multilayers

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Hydrogen evolution at a platinum microelectrode

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Due to the shift of energy production to renewable energies, it is necessary to develop novel energy storage solutions. A promising technique is the hydrogen production via water electrolysis [1]. To increase the efficiency of this method, electrode blockage by gas bubbles and the resulting increase in the cell voltage must be prevented. Therefore, the key mechanisms in bubble nucleation, growth and detachment have to be detected and analyzed.

To contribute to the understanding of this demand, we present single-bubble studies and analysis generated at a Pt microelectrode. Hydrogen evolution was performed potentiostatically from a sulfuric acid electrolyte. Special attention was given to the preparation method of the microelectrode. The quality of the surface could be identified as a major factor of reproducibility of the results and the bubble nucleation process. A visualization of the bubbles was done by a high-speed camera connected to a microscope. Bubble lifetime, size and contact angle were analyzed from the current transients and via image analysis of the videos taken.

The bubble radius increases with the polarization time while a decrease in the contact angle is detected. For long-term measurements, an increase of bubble lifetime at decreasing detachment radius is observed. Bubble size growth calculated from the current transient and the data collected by image analysis show a good correlation. The coalescence of smaller hydrogen bubbles at the bubble foot plays an important role in the growth mechanism of a single bubble [2]. After stopping hydrogen evolution, for all measurements nearly the same open circuit potential (OCP) is observed. This value relaxes until the OCP of a fresh electrode is achieved. The relaxation time is associated with the diffusion of dissolved hydrogen in the electrolyte and the decrease of the bubble size or the amount of hydrogen, respectively.

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TEM and XRD investigation of grain and defect structure in electrodeposited nanocrystalline nickel

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Electrodeposited thin films usually have a grain size in the nanocrystalline range [1], especially if some kind of organic additive is used in the electrolyte [2] since additives have an effect on the defect structure. In the present work, the effect of two kinds of organic additive (saccharin and formic acid) on the microstructure (texture, grain size, twin boundaries and dislocations) of electrodeposited Ni films was investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD) line profile analysis. Not just the average parameters of the microstructure, but the detailed distribution of grain sizes, twin boundary spacings and twin texture were also determined. New features of our work are the homogeneity investigations in both planar and cross-sectional directions, the detailed TEM measurements of the twin spacing and grain size distributions as well as the comparison of TEM and XRD results on the very same samples, both without and with additives.

In films deposited with no additive, a columnar structure with (220) texture was observed after a structure stabilization period of a few micrometer thickness, showing similarities to the T-zone of structure zone models [3]. The addition of either formic acid or saccharin resulted in nanocrystalline films with decreased grain size (20-50 nm) and increased defect density (dislocations and twin boundaries). Both effects were stronger in deposits obtained with saccharin additive. In the presence of these additives in the bath, the structure became homogeneous and free of texture throughout the total deposit thickness. Detailed grain size and twin boundary spacing distributions determined from TEM confirmed the presumptions of X-ray line profile analysis (viz. spherical grains, lognormal and geometric distributions of grain size and twin spacing, respectively). According to the cross-sectional TEM images taken on the sample deposited with saccharin, the average grain size remained constant throughout the total deposit thickness. Both films deposited with an organic additive contained numerous nano-twins [4]. Their density can be hardly measured by TEM but can be well evaluated from XRD profiles. TEM shows that twin boundaries typically span over the whole grain, have no texture and the average size of grains containing twin boundaries is two or three times larger than the average grain size.

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P-11

Revisiting the electrodeposition of Fe-Pt alloys

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Micro- and nanodimensional Fe-Pt hard magnets are still of high scientific and technological interest for data storage, micro- and nanoelectromechanical systems (MEMS/NEMS) as well as in microfluidics. In previous works, it has been demonstrated that the electrochemical co-deposition of Fe and Pt from a single aqueous electrolyte leads to an amorphous deposit containing up to 30 at.% oxygen [1]. After subsequent heat treatment, good hard magnetic properties were achieved [2], the electrolyte, however, was very unstable and could be used only once. In order to overcome these deficiencies, a new approach towards a stable Fe-Pt electrolyte and almost oxygen-free Fe-Pt deposits is presented.

By using $Fe_2(SO_4)_3$ instead of $FeSO_4$, the electroless oxidation of Fe^{2+} to Fe^{3+} by the more noble Pt ions can be completely avoided, therefore stabilizing the electrolyte. Additionally, complexation of the Fe^{3+} ions is required to prevent the formation of hydroxides and their incorporation in the deposit. Citrate or sulfosalicylic acid (SSA) are frequently used complexing agents for Fe^{3+} ions, e.g., for similar alloy systems such as Fe-Pd or Fe-Ga [3,4].

The current study presents cyclovoltammetry investigations of the complexed Fe^{3+} ions in combination with potential Pt sources such as H_2PtCl_6, $Pt(NO_2)_2(NH_3)_2$ (p-salt), and a commercially available Pt bath (JE18, Jentner Plating Technology). Fe-Pt films were then deposited from selected promising electrolyte systems. The dependence of film composition, morphology and structure on the electrolyte composition (e.g., metal ion ratio and concentrations, pH) and deposition parameter is systematically explored aiming at dense, homogeneous $Fe_{50}Pt_{50}$ films as a prerequisite for the hard magnetic $L1_0$ phase.

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Texture control and photoelectrochemical water splitting of p-Cu_2O nanowires and nanowire networks via templated electrodeposition

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For solar energy conversion into solar fuels, it is highly advantageous to use one-dimensional nanostructures as the photoactive material due to their high surface-to-volume ratio. In addition, the physical properties of most semiconductors (absorption depth and charge carrier diffusion length) demand the use of one-dimensional nanostructures to improve the transport of photogenerated charge carriers to the nanowire surface (~ tens of nm) while maintaining a sufficient "film" thickness (consisting of the nanowire length; ~ tens of µm) for optimal photon absorption [1,2].

On the search for more efficient photoelectrodes, we present the development and photoelectrochemical characterization of p-Cu_2O nanowires and nanowire networks with a relatively high texture coefficient of 4.2 (calculated from 7 peaks). Since we used polycarbonate templates fabricated by ion-track technology at the GSI linear accelerator (UNILAC) in Darmstadt for the templated electrodeposition of these nanowires and nanowire networks, we can tailor, e.g., the diameter of the final nanowires by varying the pore diameter of the templates [3]. We synthesized nanowires and nanowire networks with different diameters, and calculated the texture coefficient (TC) from X-ray diffraction (XRD) measurements performed on the nanowire arrays or networks inside the template. We found that the crystallinity of the nanowires can be tuned by variation of the nanowire diameter. This was apparent from SEM images displaying either sharp facets at the nanowire tips or a more grainy structure, and further confirmed by the TC results from XRD.

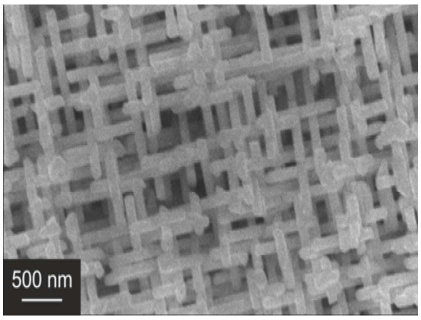

Figure 1. SEM image of a p-Cu_2O nanowire network with a nanowire diameter of 115 nm.

Nanowires consisting of larger grains would be highly advantageous as photocathodes for photoelectrochemical water splitting, offering less grain boundaries and defects, and thus resulting in lower recombination rates for the photogenerated electrons and holes. This would significantly improve the overall efficiency of the system.

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P-13

Biomimetic, self-cleaning metal coatings with superimposed micro- and nanoscale roughness

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We show how superhydrophobic metal coatings can be created using redox-chemical deposition methods in conjunction with a biomimetic design strategy. Previous studies indicate that the special topography of the lotus leaf, which is characterized by a hierarchic roughness on the micro- and nanoscale [1], can be mimicked to create artificial coatings with self-cleaning properties [2].

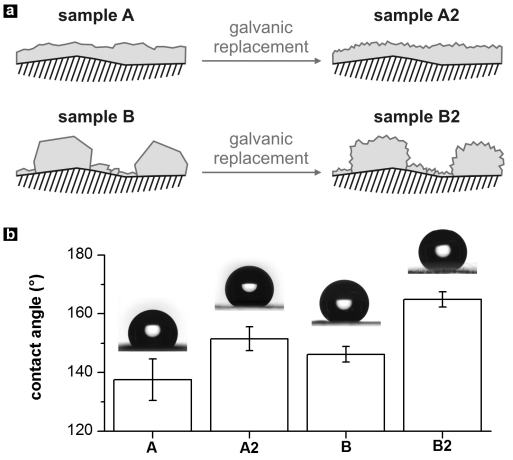

Figure 1. a) Morphological scheme of four metal coatings with differing roughness features, and b) their respective water contact angles.

To evaluate the role of the topography, we synthesized a set of surfaces with defined roughness features. First, electroless Ag plating was adjusted to produce either relatively smooth metal films or metal films containing microparticle islands. These two surface types were then optionally subjected to a moderated galvanic replacement reaction, which leads to a nanoscale roughening of the metal films. Subsequently, the surface energy of the four coating types was reduced with thiol self-assembly. The hydrophobicity of the resulting materials was examined by placing water droplets on them, followed by measuring the static contact angle, the roll-off angle and the drop hysteresis. The weakest interaction with water was found for the material with a pronounced, superimposed micro- and nanoscale roughness. This surface is characterized by a very high contact angle of 165°, a tilt angle of < 3° and a neglectable drop hysteresis. The outlined process can be applied to arbitrarily shaped substrates and is interesting for the fabrication of multifunctional materials such as superhydrophobic, antibacterial and electrically conducting textiles [3].

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Electrodeposition of Ni from various non-aqueous media: the case of alcoholic solutions

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Although electrodeposition from aqueous media has been widely used to obtain metallic deposits, there are cases where the application of non-aqueous solutions offers advantages over the traditional baths or it even represents the only way to electrodeposit some metals.

A study of the electrodeposition of Ni from various alcoholic solutions was performed [1]. Besides methanol and ethanol as solvents, Ni electrodeposition from ethylene glycol, glycerol, 1,2-propanediol and 1,3-propanediol was also the aim of our research.

A detailed cyclic voltammetry study of these solutions has been carried out by establishing the polarization characteristics of Ni deposition and dissolution in each bath. Then the surface morphology, crystal structure and texture as well magnetic properties of the deposits have also been investigated.

The best results were obtained with methanol as solvent and the deposit quality was investigated for various deposition potentials. Compact Ni deposits with metallic appearance and nanocrystalline grain size were obtained in the deposition potential range of –1.10 V to –1.40 V vs. SCE. A weak (111) texture of the deposits was observed by XRD and the lattice constant corresponded well to pure face-centred cubic (fcc) Ni.

From the other solvents investigated, the Ni deposits were of lower quality in most cases. The Ni content in the deposits was in some cases fairly low and the characteristic fcc-Ni lines could also not always be observed.

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P-15

Adjusting the Fe-Ga deposition to enable nanowire preparation

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Due to their high magnetostriction and excellent mechanical properties, Fe-Ga alloys are of increasingly high interest for sensor and actuator applications [1,2]. Low-dimensional structures with complex geometries as required for further miniaturization are accessible by electrochemical deposition. Thin films of $Fe_{80}Ga_{20}$ were successfully prepared from a simple aqueous electrolyte [3-5]. EQCM measurements reveal that an induced co-deposition of Fe and Ga takes place while simultaneously huge amounts of oxidic species are formed and incorporated in the deposit. Introducing a pulse-plating regime with a second, more positive "relaxation" potential allows a redissolution of the oxidic species. The remaining layer is a pure alloy film. The resulting $Fe_{80}Ga_{20}$ alloy layer is homogeneous, dense and shows negligible oxygen content at the interface to the substrate.

In order to reduce the dimensionality, nanowires were deposited within nanoporous templates. It has been shown that, for sub-micrometer pore diameters, the simple electrolyte allows to completely fill the pores and to produce metallic nanowires. At pore diameters below 100 nm, the restricted transport properties in the narrow-pore geometry limit the growth of continuous nanowires [5]. The strong hydrogen evolution produces large amounts of hydroxides that cannot be completely re-dissolved and removed from the high-aspect-ratio nanopores. The resulting nanowires are discontinuous and show a composition gradient along the growth direction. Using EQCM analysis, we will show that the addition of a complexing agent influences the deposition behavior in this binary system. By modifying the electrolyte, the hydroxide formation and incorporation can be almost completely prevented [5]. This knowledge enables the deposition of nanowires with a length of several micrometers even at pore diameters below 100 nm. They are continuous, dense and do not show a composition gradient along the wire axis. Detailed TEM investigations reveal only minor differences between wires prepared by pulse plating or potentiostatic deposition. Surprisingly, potentiostatic deposition yields even better nanowire microstructure and less pronounced stress patterns.

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Template-based synthesis of Pt-coated magnetic nanostructures and their application as recyclable catalysts for nitrophenol reduction

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One-dimensional magnetic nanostructures,uch as metal nanowires, nanorods or nanotubes became of major interest over the last years. The reason for that is the possibility to increase the storage density of hard disk drives. Despite this common field of application, magnetic nanostructures can also be used in sensor technology, catalysis, transportation or separation processes. Especially the field of recyclable catalysts is a very promising field for magnetic structures in terms of economic and enironmental considerations [1,2]. Ferromagnetic metals like Ni and Co can act as catalyst for themselves [3] but furthermore they can also be used as supporting material for more active catalytic materials such as Pt or Pd [4]. These metals are deposited on the surface of the magnetic nanostructure, which are used as sacrificial template for galvanic replacement reactions. This method opens up a possible way to construct highly active and recyclable catalysts.

First of all, it is necessary to synthesize magnetic 1D nanostructures by electrodeposition or electroless plating. Depending on the deposition method, two different sacrificial template types can be synthesized. Nanowires are produced by electrodeposition, whereas nanotubes are synthesized via electroless plating. By using a galvanic replacement reaction, the surface of the magnetic nanostrucure is enriched with, e.g., Pt, which can be controlled by the reaction conditions. Other possible strategies for noble metal doping include superficial decoration with nanoparticles or the deposition of multilayer structures. We present different (bi)metallic catalysts prepared with electroless plating (nanotubes), electrodeposition (nanowires) and additional reactions such as galvanic replacement, and evaluate their performance in a model reaction, the reduction of 4-nitrophenol. The magnetic nature of these materials allows us to recapture the catalyst by applying an external magnetic field. It is possible that the recycling process influences the activity of the catalyst, which is investigated as well.

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P-17

Tuning The Magnetic Properties Of Multisegmented Ni/Cu Electrodeposited Nanowires With Controllable Ni Lenghts

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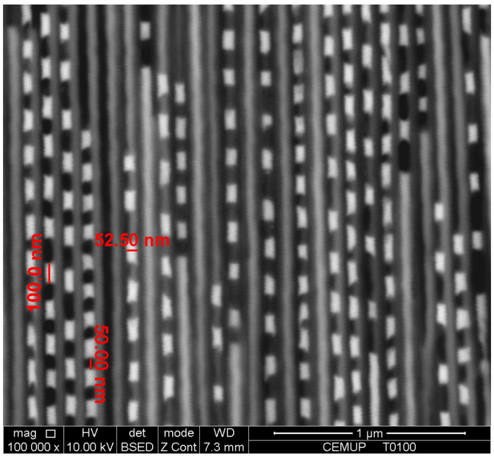
The fabrication of segmented Ni/Cu nanowires (NWs), with suitable structural and magnetic properties for several applications, is reported. A potentiostatic electrodeposition method with a single electrolytic bath has been used to fabricate multisegmented Ni/Cu NWs inside a highly hexagonally ordered anodic nanoporous alumina membrane, with diameters and Cu segment lengths of 50 nm and Ni segment lengths (L_{Ni}) tuned from 10 nm up to 140 nm. As determined by X-ray diffraction, Ni/Cu NWs with $L_{Ni} > 70$ nm present a crystallographic fcc structure strongly textured along the <220> direction, while for $L_{Ni} = 20$ nm and $L_{Ni} = 45$ nm a fcc lattice with a <111> preferred direction is obtained, proving the relation between Ni segments length and texture [1]. The magnetic behavior of the multisegmented Ni/Cu NW arrays, as a function of the magnetic field and temperature, is also studied and correlated with their structural and morphological properties. We found that the coercivity, remanence and Curie temperature of the NWs are strongly dependent on the Ni magnetic segment length and on the respective chemical composition [2]. When decreasing L_{Ni}, both the Curie temperature and the coercivity measured parallel to the NW axis were found to decrease. These results emphasize the advantages of using a template assisted method to electrodeposit multilayer NWs, as it allows an easy tailor of the respective morphological, chemical, structural and magnetic properties.



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Challenges of the electrodeposition of delafossites

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The continuously growing concentration of atmospheric carbon dioxide necessitates urgent steps in this field. Solar fuel generation is an attractive approach, because in addition to the reduction of the carbon dioxide quantity, fuel materials are produced in this process. For the photoelectrochemical reduction of CO_2, p-type semiconductor electrodes are required. Oxide semiconductor photocathodes are attractive candidates in this manner.

One of the mostly studied material in this vein is Cu_2O, which shows excellent performance in this process. However, the lack of its long term stability limits its application. Therefore, a more stable class of semiconductors with the chemical structure of $CuXO_2$ (where X: Fe^{3+},Cr^{3+},Rh^{3+},Al^{3+} etc.) attracts significant interest nowadays. Based on their low bandgap (which is between 1.3-2.0 eV) and its proper position, they can absorb large part of the visible spectrum and have the potential for carbon dioxide reduction.

These materials are usually prepared by solid state reaction which makes them very expensive. Electrochemical methods offer a mild way to make their synthesis much more affordable. Electrochemical reduction of Cu^{2+} ions in the presence of the X^{3+} ion leads to the formation of $CuXO_2$ structured semiconductors. One of the most studied member of these materials ($CuFeO_2$) has already been deposited from DMSO.

However, it’s a challenging task to deposit this material from benign aqueous media. In this media, the effect of pH should be considered, because at the pH where Cu^{2+} can be reduced to Cu^{+}, the possibility of hydroxide formation can prevent the deposition of delafossites. In addition, the ratio of Cu:X is greatly influenced by the applied potential.

In my poster presentation, I will show how the proper parameters can be selected to form delafossites with desired composition from Pourbaix diagrams of aqueous solution. The effect of different circumstances (potential, different anions) on the Cu:X ratio of the formed delafossites will be discussed . These findings are based on measurements with Raman, XRD and EDX spectroscopy.

P-19

Development of nanowire based structures of bismuth and antimony for thermoelectric applications

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We present the development of nanowire arrays and networks of Bi and Sb for thermoelectric applications [1,2]. Calculations predict that by using the unique size-dependent properties of nanowires, nanowire-sensors with significantly faster response, higher sensitivity, detectivity, and spatial resolution than their thin film counterparts can be fabricated [3]. The nanowire structures are prepared by electrodeposition in the pores of etched ion-track membranes. To prepare the templates, polycarbonate foils are irradiated with swift heavy ions at the linear accelerator of the GSI Helmholtz Center, and the ion tracks are subsequently etched in a concentrated NaOH solution. Templates with both parallel and interconnected nanochannels are produced by adjusting the irradiation conditions. Achieving a homogeneous filling of the pores is critical for future device integration and characterization. This is achieved by applying pulsed electrodeposition. The influence of wire diameter and density on the mechanical stability and interconnectivity of the obtained networks is visualized by scanning electron microscopy. First measurements of the Seebeck coefficient, electrical- and thermal conductivity of networks will be discussed [4].

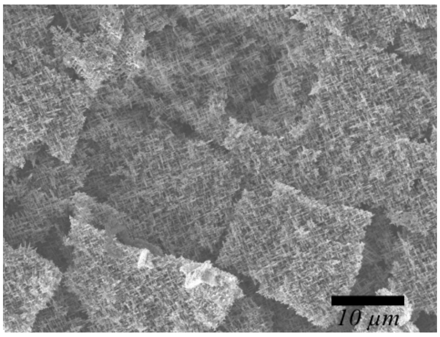

Figure 1. $Bi_{1-x}Sb_x$ nanowire network

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Bimetallic catalysts for ORR and EOR

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Actually, platinum is still the most common metal catalyst in both anode and cathode fuel cell. In spite of the many attempts made in the last decade to develop non-Pt based catalysts for low temperature air cathodes, Pt remains the catalyst of choice, at least for acid-based fuel cells. The situation in alkaline electrolytes is rather different; due to the stability of non-noble metals in this environment, many more opportunities are available for the development of non-Pt catalysts for the Oxygen Reduction Reaction (ORR) and for the Ethanol Oxidation Reaction (EOR). To completely remove Pt and to replace it with less expensive materials, bimetallic electrocatalysts have been proposed to exploit a synergic mechanism with one metal able to break the O-O bond of the molecular oxygen at the cathode side and the second metal effective in reducing the adsorbed oxygen so formed [1]. At the same time, the Pd-based catalysts in alkaline-type DEFCs can be an alternative to the Pt-based catalysts for the alcohol oxidation reactions in alkaline media [2]. In this contest, we studied the contribution of two binary catalysts against ORR and EOR: silver and cobalt, whose catalytic activity against ORR has been reported long ago [3-5] were combined together by electrodeposition on a glassy carbon electrode. The activity of the small amount of the binary Ag-Co catalyst (17 µg cm^{-2}) was compared with the catalytic activity of the only-silver deposits that had given the best catalytic effect in Ref 6. Rotating ring electrode measurements were performed to estimate the average number of exchanged electron during the reaction. On the other hand ,the catalytic activity of a Pd-Co alloy against EOR was estimated. The Pd-Co samples were grown by co-deposition on a Si/Au electrode and the increasing amount of Co was correlated with the increasing catalytic property of the samples. An unusual change of the morphology on the Co-rich sample was observed during the cyclic voltammetry study due to a partial dissolution and deposition of the same metal.

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Saturday 12 September 2015	
	EXCURSION: route and programmes
9^{00} – 10^{00}	Walking from Hotel Margaréta to Balatonfüred port
10^{00} – 10^{20}	Boat trip to Tihany port
10^{20} – 10^{50}	Trip up to Tihany village/Abbey by trackless road train (Dotto train)
10^{50} – 12^{15}	Visit of Tihany village and Abbey
12^{15} – 12^{40}	Bus trip to Révfülöp
12^{40} – 14^{15}	Lunch at Révfülöp, Restaurant Hangulat
14^{15} – 14^{40}	Bus trip to Badacsony
14^{40} – 15^{45}	Sightseeing in Badacsony, visiting museum
15^{45} – 16^{45}	Wine tasting
16^{45} – 17^{45}	Bus trip to Balatonfüred, Hotel Margaréta
18^{00} – 19^{00}	Free time (dinner at your hotel, *not included in the excursion*)
19^{00} – 21^{00}	Evening walking tour in Balatonfüred

Map of Balaton with location of places to be visited during the excursion

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