

12th INTERNATIONAL WORKSHOP ON ELECTRODEPOSITED NANOSTRUCTURES (EDNANO - 12)

PROGRAMME BOOK OF ABSTRACTS

March 16-18, 2017 Sofia, Bulgaria



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Host organization: Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria http://ipc.bas.bg/page/en/home.php



EDNANO – 12 Local Organizing Committee

Tsvetina Dobrovolska, Vessela Tsakova, Dessislava Guergova, Vasil Bachvarov, Nina Dimitrova, Vasil Kostov



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

EDNANO Board members

Joao Pedro ARUJO DE ESTEVES, University of Porto, Portugal Imre BAKONYI, Wigner Research Centre for Physics, Budapest, Hungary Horia CHIRIAC, National Institute of R&D for Technical Physics, Iasi, Romania Wolfgang HANSAL, Happy Pating GmbH, Wiener Neustadt, Austria László PÉTER (secretary), Wigner Research Centre for Physics, Budapest, Hungary Sudipta ROY, University of Strathclyde, Glasgow, UK Walther SCHWARZACHER, University ofBristol, UK Ibro TABAKOVIC, University of Minnesota, Minneapolis, USA Margitta UHLEMANN, IFW Dresden, Germany Giovanni ZANGARI, University of Virgina, Charlottesville, USA

URL of EDNANO homepage www.szfki.hu/ednano

Aims and Objectives

The aim of the EDNANO-12 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 this time that we will also have a lot of interesting presentations of different topics.

Scientific programme

The scientific programme of the EDNANO-12 workshop includes 25 oral presentations each of 20 minutes length including a short discussion time. The speakers are marked by underlining in the list of oral contributions which were assigned to 6 consecutive scientific sessions each of 3-6 presentations. A poster session will also be held at the end of the first day of the workshop; currently, we have abstracts for 28 posters. 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-12 workshop helds in the Sofia, the capital and largest city of Bulgaria. For the longest time the city possessed Thracian name, derived from the tribe Serdi. The city has a history of nearly 7000 years and the motto of the city is "grows, but does not age". Sofia is located at the foot of Vitosha Mountain in the western part of the country. Sofia as a capital is the location of all Bulgarian state authorities – executive, legislative, judiciary, this includes the Parliament, the Presidency, the Council of Ministers and all the ministries.

Rostislaw Kaischew Institute of Physical Chemistry (IPC) as a part of Bulgarian Academy of Sciences, is founded in 1958 to carry out fundamental and applied scientific research in the field of physical chemistry.

The venue of the workshop is Arena Di Serdica, located in downtown Sofia with an elegant modern facility, which hosts one of Sofia's most precious treasures – the remains of the roman Amphitheatre of Ancient Serdica, which date back to the III-IV century. Next to Sofia's main cultural sights and institutions, the Arena di Serdica Hotel offers the perfect setting for both business and leisure.

Social programme

In addition to a welcome reception (Wednesday evening) and workshop banquet (Thursday evening) for all participants, there will be also a tour to the Plovdiv and Starosel.



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TECHNICAL PROGRAMME

DATE: 15 MARCH 2017

18:00 – 19:00 REGISTRATION Welcome party at Hotel Arena di Serdica, Sofia

DATE: 16 MARCH 2017

8:00 – 8:45 REGISTRATION 8:50 – 9:20 OPENING SESSION

SESSION I

Chairperson: László Péter

(Wigner Research Centre for Physics, Hungary)

9:20 - 9:40

Nanostructures where the active component is a single-molecule

R. J. Brooke¹, A. Vezzoli², S. J. Higgins², R. J. Nichols², <u>Walther Schwarzacher</u>¹* ¹H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL UK ²Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UK

9:40 - 10:00

Nanostructure design for photocatalytic water splitting

Wouter Maijenburg

ZIK SiLi-nano / MLU Halle-Wittenberg, Karl-Freiherr-von-Fritsch-Straße 3, 06120 Halle (Saale), Germany

10:00-10:20

Electroless deposition of metals on conducting polymer layers

<u>Vessela Tsakova</u>*, A. Nakova, V. Karabozhikova, M. Ilieva, V. Lyutov Institute of Physical Chemistry, Bulgarian Academy of Siences, 113 Sofia, Bulgaria

10:20 - 10:40

Electrodeposited Cu_2O nanowire arrays and networks as photocathode model systems for solar hydrogen production

<u>Florent Yang</u>^{1*}, Jan Kugelstadt¹, Liana Movsesyan¹, Wouter Maijenburg^{1,2}, Christina Trautmann¹, Maria Eugenia Toimil-Molares^{1*}

¹GSI Helmholtz Centre for Heavy Ion Research, Department of Materials Research, Planckstraße 1, 64291 Darmstadt, Germany

²Martin Luther University Halle-Wittenberg, Halle, Germany

COFFEE BREAK: 10:40 – 11:10

SESSION II

Chairperson: Celia Tavares de Sousa (Universidade do Porto, Porto, Portugal)

11:10 - 11:30

Lithium versus Sodium Intercalation: Energy Storage beyond Lithium-Ion Batteries Radostina Stoyanova* and E. Zhecheva

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

11:30 - 11:50

Determining the diffusion mechanism for high aspect-ratio ZnO nanowires electrodeposited into anodic Aluminum oxide

Cristina Manzano*, L. Pethö, J. Michler, L. Philippe

Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland

11:50 - 12:10

Three-Dimensional Porous Alumina Networks on Cylindrical Aluminum

Pedro Resende, Ruy Sanz, Alejandra Ruiz-Clavijo, Olga Caballero-Calero, Marisol Martín-González

Instituto de Microelectrónica de Madrid (IMM-CSIC), Calle de Isaac Newton 8, Tres Cantos, 28760 Madrid, Spain

12:10 - 12:30

Understanding the Fe-Ga deposition in aqueous electrolytes for template based nanowire preparation

Diana Pohl (Iselt)^{1,2*}, K. Tschulik³, Ch. Damm¹, L. Schultz¹, H. Schlörb¹ ¹IFW Dresden, P.O. Box: 270116, 01171 Dresden, Germany ²TU Dresden, Faculty of Mechanical Engineering, 01062 Dresden, Germany ³Ruhr-Universität Bochum, 44780 Bochum, Germany

LUNCH: 12:30 - 14:00

SESSION III

Chairperson: Piotr Zabinski (University of Science and Technology, Kraków)

14:00 - 14:20

Electrodeposition of $Bi_{1-x}Sb_x$ nanowire networks and determination of their Seebeck coefficient

Michael Wagner^{1,2,*}, S. Paulus^{1,2}, P. Kuhn^{1,2}, J. Brötz², C. Trautmann^{1,2}, K.-O. Voss¹, M.E. Toimil-Molares^{1,*}

¹Materials Research Department, GSI Helmholtz Center, Planckstr. 1, 64291 Darmstadt, Germany ²Technische Universität Darmstadt

14:20 - 14:40

Seebeck coefficient enhancement in electrodeposited $Bi_2Te_{3-y}Se_y$ films with additives and pH variations on the electrochemical bath

<u>Olga Caballero-Calero¹</u>, Diana-Andra Borca-Tasciuc², András Gorog¹, Theodorian Borca-Tasciuc², Marisol Martín-González¹

¹Instituto de Microelectrónica de Madrid (IMM-CSIC), Calle de Isaac Newton 8, Tres Cantos, 28760 Madrid, Spain

²Mechanical, Aerospace and Nuclear Engineering Department, Rensselaer Polytechnic Institute Troy, New York 12180, USA

14:40 - 15:00

Tuning the morphology of tellurium nanostructures by template-free electrodeposition in ionic liquids: from hollow nanostructures to hair-like nanowires

L. Thiebaud, <u>Sophie Legeai</u>, J. Ghanbaja, N. Stein Institut Jean Lamour – Joint Laboratory UMR 7198 University of Lorraine – CNRS 1 bd Arago -57078 Metz Cedex 3, France

15:00 - 15:20

Shape-controlled electroless plating of Silver nano-platelet films

Falk Muench^{1,2*}, Alexander Vaskevich¹, Israel Rubinstein¹

¹Weizmann Institute of Science, Department of Materials and Interfaces, Herzl Street 234, 7610001 Rehovot, Israel

²Technische Universität Darmstadt, Deparment of Materials and Earth Sciences, Alarich-Weiss-Street 2, 64287 Darmstadt, Germany

15:20 - 15:40

Jenia Georgieva^{1*}, E. Valova¹, S. Armyanov¹, D. Tatchev¹, S. Sotiropoulos², N. Dimitrova¹ Institute of Physical Chemistry, Bulgarian Academy of Siences, 113 Sofia, Bulgaria

²Department of Chemistry, Aristotle University of Thessaloniki, Greece

COFFEE BREAK: 15:40 – 16:30
POSTER SESSION: 16:30 – 18:30
BANQUET DINNER: 20:00 – 22:00

POSTER SESSION (16 March 2017, 16:30 – 18:30)

P - 1

Electrodeposited NiSn coating as the catalysts for alkaline water electrolysis

B.M. Jović¹, U.Č. Lačnjevac¹, N.V. Krstajić², <u>Nevenka Elezović</u>¹, P.Zabinski³, Lj. Gajic-Krstajić⁴, V.D. Jović¹

¹Institute for Multidisciplinary Research University of Belgrade, P.O. Box 33, 11030 Belgrade, Serbia

²Faculty of Technology and Metallurgy University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia,

³2AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Al. Mickiewicza 30,30-059 Krakow, Poland

⁴Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35, Belgrade, Serbia

P - 2

EDNANO12

Comparative analysis of chemically and electrochemically produced silver powders of nanostructural characteristics

<u>Nikolić Nebojša</u>^{1*}, Avramović Lj.², Maksimović V.M.³, Pavlović M.M.¹, Pršić S.⁴, Stevanović J.¹, Bugarin M.²

¹ICTM-Department of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia ²Mining and Metallurgy Institute, Zeleni bulevar 35, Bor, Serbia

³Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

⁴Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1a, Belgrade, Serbia

P - 3

The morphology of Zn-Mn electrodeposits obtained from choline chloride-urea deep eutectic solvent

Sanja Stevanovic¹, Mihael Bucko², Jelena Bajat^{3*}

¹ICTM – IEC, P.O. Box 473, 11001 Belgrade, Serbia

²Military Academy, University of Defence, Belgrade, Serbia

³Faculty of Technology and Metallurgy, University of Belgrade, P.O. Box 3503, 11120 Belgrade, Serbia

P – 4

Effects of selected additives by the electrodeposition of Pd films from non-aqueous solutions <u>Mila Manolova</u>, R. Boeck

fem – *research institute for precious metals & metals chemistry, Department of electrochemistry, corrosion and electroplating*

P – 5

MOF and metal oxide nanostructures for photocatalytic water splitting

<u>Ana María Araújo Cordero</u>^{1*}, Titus Lindenberg^{1*}, A. Wouter Maijenburg¹ ¹ZIK SiLi-nano / MLU Halle-Wittenberg, Karl-Freiherr-von-Fritsch-Straße 3, 06120 Halle (Saale), Germany

P – 6

Increasing the compositional complexity of nanotubes and nanotube networks.

<u>Falk Muench^{1,2*}</u>, Luwan Sun², Tobias Stohr², Sandra Schaefer², Markus Antoni², Wolfgang Ensinger²

¹Weizmann Institute of Science, Department of Materials and Interfaces, Herzl Street 234, 7610001 Rehovot, Israel

²Technische Universität Darmstadt, Deparment of Materials and Earth Sciences, Alarich-Weiss-Street 2, 64287 Darmstadt, Germany

$\mathbf{P} - \mathbf{7}$

Electrochemical deposition of CoNi-PPy composite structures by changing Co concentration Dilek Vatansever¹, <u>Murside Haciismailoglu</u>^{1*}, Mursel Alper¹, Hakan Kockar²

¹University of Uludag Faculty of Science and Literature Department of Physics 16059 Gorukle Bursa Turkey

²University of Balikesir Faculty of Science and Literature Department of Physics 10145 Cagis Balikesir Turkey



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Structural and optical properties of electrodeposited NiO thin films

Cigdem Epiri^{1,2}, <u>Murside Haciismailoglu</u>^{1*}, Mursel Alper¹, M. Cuneyt Haciismailoglu ¹University of Uludag Faculty of Science and Literature Department of Physics 16059 Gorukle Bursa Turkey

²FARBA A.Ş., Organize Sanayi Bölgesi, Sarı Cadde, No:21, Nilüfer, 16140 Bursa, Turkey

P - 9

Electron microscopy analysis and magnetic characterization of Ni-Co/Cu multilayered nanowires grown in AAO membranes

S. Zsurzsa¹, <u>Imre Bakonyi</u>^{1*}, L. Péter¹, J. Sort², E. Pellicer²

¹Wigner Research Centre for Physics, Hungarian Academy of Sciences. H-1121 Budapest, Konkoly-Thege út 29-33, Hungary

²Autonomous University of Barcelona (UAB), E-08193 Bellaterra, Spain

$\mathbf{P}-\mathbf{10}$

Morphology of the self-organized copper-antimony electrodeposited alloy

Vasil Kostov, I. Krastev, Ts. Dobrovolska

Institute of Physical Chemistry, Bulgarian Academy of Siences, 113 Sofia, Bulgaria

P-11

Spatio-temporal structures of electrodeposited indium based alloys

Tsvetina Dobrovolska¹, U. Lačnjevac², N. Tasic², N. Elezovic²,

¹Institute of Physical Chemistry, Bulgarian Academy of Siences, 113 Sofia, Bulgaria

²Institute for Multidisciplinary Research University of Belgrade, P.O. Box 33, 11030 Belgrade, Serbia

P - 12

Comparative studies of electroless and electrochemically deposited ceria layers on Aluminum

<u>Reni Andreeva</u>^{1*}, Desislava Guergova¹, Emilia Stoyanova¹, Genoveva Atanasova², Dimitar Stoychev¹

¹Institute of Physical Chemistry, Bulgarian Academy of Siences, 113 Sofia, Bulgaria ²Institute of General and Inorganic Chemistry, Laboratory of Electron Spectroscopy of Solid Surfaces

P – 13

Electrocatalytic activity of ternary Ni-Co-Cu and Ni-Mo-Cu alloys for hydrogen evolution reaction in alkaline area

Desislava Goranova, R. Rashkov

Institute of Physical Chemistry, Bulgarian Academy of Siences, 113 Sofia, Bulgaria

P – 14

Obtaining of protective zinc composite coatings with environmentally friendly conversion films

Miglena Peshova, V. Bachvarov, St. Vitkova, N. Boshkov

Institute of Physical Chemistry, Bulgarian Academy of Siences, 113 Sofia, Bulgaria



P – 15

Anticorrosion zinc coating containing "smart" core-shell nanocontainers with benzotriazole Kamelia Kamburova, Nelly Boshkova, N. Boshkov, Ts. Radeva

Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

P - 16

Electroless deposition of Copper thin layers on ABS structures

<u>Mihaela Georgieva</u>^{1*}, Veselina Chakarova¹, Maria Petrova¹, Ekaterina Dobreva², Nadia Koteva² ¹Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria ²Technical University – Sofia, Bulgaria

P – 17

$Electroless \ deposition \ of \ palladium \ nanoparticles \ on \ polysterensulfonate-doped \ poly (3, 4-ethyeledioxythiophene) - role \ of \ the \ electrode \ substrate$

<u>Aneliya Nakova¹</u>, M. Ilieva¹, Tz. Boiadjieva-Scherzer², V Tsakova^{1*}

¹Institute of Physical Chemistry, Bulgarian Academy of Siences, 1113 Sofia, Bulgaria ²CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Wiener Neustadt, Austria

P – 18

Preparation and characterization of B and N co-doped TiO_2 nanotube arrays with enhanced photoelectrochemical performance

Jenia Georgieva^{*1}, <u>Nina Dimitrova</u>¹, Stephan Armyanov¹, Eugenia Valova¹, Dragomir Tatchev¹, Sotiris Sotiropoulos²

¹Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria ²Department of Chemistry, Aristotle University of Thessaloniki, Greece

P - 19

Fabrication of 1D, 2D, and 3D periodic magnetic nanostructures using (electro)chemical approaches

<u>Heike Schlörb</u>¹, K. Leistner¹, J. Garcia¹, A. Niemann¹, M. Uhlemann², K. Nielsch¹ Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research Dresden

²Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research Dresden ²Institute for Complex Materials, Leibniz Institute for Solid State and Materials Research Dresden Helmholtzstr. 20, 01069 Dresden, Germany

P - 20

Lithographically guided electrodeposition of BiTe-based micro-thermoelectric coolers

J. García, M. Mohn, N. Pérez-Rodriguez, D. Lara-Ramos, <u>Heike Schlörb</u>, H. Reith, G. Schierning, K. Nielsch

Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research Dresden

P – 21

Electrodeposited micromagnets for microfluidic applications

<u>Veronika Haehnel</u>^{1,*}, C. Konczak¹, J. König², H. Schlörb¹, M. Uhlemann¹, K. Nielsch¹ ¹*IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany* ²*Tachningha Universität Umengu, P.O. Pop. 100565, 08684 Umengu, Carrage*

²Technische Universität Ilmenau, P.O. Box 100565, 98684 Ilmenau, Germany

P – 22

Morphologic and Crystalline structure of Bi-Te based nanomaterials by electrodeposition M.P. Proenca^{1,2}, M. Rosmaninho¹, P.M. Resende¹, C.T. Sousa¹, J. Ventura¹, <u>Joao Pedro Araújo¹</u>, L. Fernandes³, P.B. Tavares³, A.M. Pereira¹

¹IFIMUP and IN-Institute of Nanoscience and Nanotechnology, Dep. Física e Astronomia, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

²Instituto de Sistemas Optoelectrónicos y Microtecnología (ISOM), Universidad Politécnica de Madrid, Avda. Complutense s/n, E-28040 Madrid, Spain

³Departamento de Química, CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

P – 23

H₂ evolution on Pt microelectrodes under the influence of magnetic fields

<u>Franziska Karnbach^{1,2*}</u>, Margitta Uhlemann¹, Xuegeng Yang³, Kerstin Eckert³, Dominik Baczyzmalski⁴, Christian Cierpka⁵, Gerd Mutschke³, Annett Gebert¹

¹IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, D-01069 Dresden, Germany

²TU Dresden, Faculty of Mechanical Science and Engineering, D-01062 Dresden, Germany

³HZDR Dresden Rossendorf, Institute of Fluid Dynamics

⁴Universität der Bundeswehr München, Institute of Fluid Mechanics and Aerodynamics

⁵Technische Universität Ilmenau, Institute of Thermodynamics and Fluid Mechanics

P – 24

Indenter tip calibration at shallow depths for mechanical characterization of thin films

<u>Nelly Nikolova¹</u>, <u>Roussislava Zaharieva-Georgieva</u>^{2*}, Maria Datcheva², Dimitar Stoychev¹ ¹Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria ²Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 4, 1113 Sofia, Bulgaria

P - 25

The influence of water on the cathodic voltammetric responses of choline chloride-urea and choline chloride-ethylene glycol deep eutectic solvents

Sudipta Roy¹, Priscila Valverde Armas¹, Mihael Bucko², Jelena Bajat^{3*}

¹Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, UK

²Military Academy, University of Defense, Belgrade, Serbia

³Faculty of Technology and Metallurgy, University of Belgrade, P.O. Box 3503, 11120 Belgrade, Serbia

P - 26

Instabilities during electrochemical deposition of Sn-Co alloy from gluconate/sulfate electrolyte Teodora Valkova, I. Krastev

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

P – 27

Selective Metallization of Laser Irradiated Biocompatible poly(dimethylsiloxane). Electroless Ni deposition

Stephan Armyanov^{1*}, <u>Eugenia Valova</u>¹, Konstantin Kolev¹, Jenia Georgieva¹, Dragomir Tatchev¹, Petar Atanasov², Nadya E. Stankova²

¹Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

²Institute of Electronics, Bulgarian Academy of Sciences, Sofia 1784, Bulgaria

P - 28

Effect of anodic aluminium oxide structure on the electroless nickel deposition into nanopores Boriana Tzaneva^{1*}, N.-B. Bercu², M. Molinari², V. Videkov¹

¹Technical University of Sofia/Department of Chemistry (Kl. Ohridski Blvd. 8, 1000 Sofia, Bulgaria)

²University of Reims Champagn Ardenne/Laboratory of Nanosciences

³Technical University of Sofia/Department of Microelectronics

P – 29

All-electrochemical approach towards ON/OFF switching of magnetism in FeO_X/Fe nanostructures at room temperature

Kenny Duschek¹, Andreas Petr¹, <u>Margitta Uhlemann</u>¹, Kornelius Nielsch^{1,2} and Karin Leistner^{1,2*} ¹*IFW Dresden, Helmholtzstr. 20, D-01069 Dresden, Germany*

²TU Dresden, Faculty of Mechanical Engineering, Institute of Material Science, D-01062 Dresden, Germany

$\mathbf{P}-\mathbf{30}$

ZnO/TiO₂ Core/shell Nanowire Networks Fabricated by Ion-track Technology and Atomic Layer Deposition

<u>Mercedes Carrillo-Solano</u>¹, L. Movsesyan^{1,2}, C. Trautmann^{1,2} and M. E. Toimil-Molares¹ ¹GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt, Germany ²Material und Geowissenschaften, Technische Universität Darmstadt, Darmstadt, Germany

FRIDAY: 17 MARCH 2017

SESSION IV

Chairperson: Maria-Eugenia Toimil-Molares

(Helmholtz Centre for Heavy Ion Research, Darmstadt, Germany)

9:00 - 9:20

Glow discharge – time-of-flight mass spectrometric composition depth profile study of electrodeposited Ni-Cu/Cu multilayers

Katalin Németh¹, Rocío Muñíz Delgado², Lara Lobo², Rosario Pereiro², László Péter^{1*}

¹Wigner Research Centre for Physics, Hungarian Academy of Sciences Konkoly-Theget út 29-33, H–1121 Budapest, Hungary

²University of Oviedo, Dept. of Physical and Analytical Chemistry; Oviedo, Spain

9:20 - 9:40

Copper and copper oxide nanoparticles: A plasmonic perspective

<u>Alexander Vaskevich</u>^{1*}, Mariano D. Susman¹, Yishai Feldman², Tatyana B. Bendikov², Israel Rubinstein¹

¹Departments of Materials and Interfaces and

²Chemical Research Support, Weizmann Institute of Science, Rehovot 7610001, Israel

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9:40 - 10:00

Tuning the magnetic properties of multisegmented Ni/Cu electrodeposited nanowires with controllable Ni lengths

Célia Tavares de Sousa^{1*}, M Susano¹, M P Proenca^{1,2}, S Moraes¹, and J P Araújo¹

¹*IFIMUP* and *IN-Institute* of Nanoscience and Nanotechnology and Dep. Física e Astronomia, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal.

²Instituto de Sistemas Optoelectrónicos y Microtecnología, Universidad Politécnica de Madrid, Avda. Complutense s/n, E-28040 Madrid, Spain

10:00 - 10:20

Electrodeposition of morphological selected nano metal deposits and Pd films from ionic liquids

Reinhard Boeck

fem – *research institute for precious metals & metals chemistry. Department of electrochemistry, corrosion and electroplating*

10:20 - 10:40

Electrodeposition of Co nanowires from deep eutectic solvents (DESs) and analogous Gabriele Panzeri, Matteo Tresoldi, Luca Magagnin

Dip. Chimica, Materiali e Ing. Chimica G. Natta – Politecnico di Milano; Via Mancinelli, 7 – 20131 Milano (Italy)

COFFEE BREAK: 10:40 – 11:10

SESSION V

Chairperson: Walther Schwarzacher (University of Bristol, Bristol, UK)

11:10 - 11:30

Electrodeposition of cobalt-ruthenium alloys from acidic chloride ions containing baths D. Kutyla, K. Kolczyk, R. Kowalik, <u>Piotr Żabinski</u>

AGH University of Science and Technology, Faculty of Non-Ferrous Metals, al. Mickiewicza 30, 30-059 Kraków

11:30 - 11:50

Tailoring the magnetization direction in electrodeposited Fe-Pd and Co-Pt nanowires $V_{ricting}$, $\tilde{Z}_{virting}$, \tilde

<u>Kristina Žužek Rožman^{1,2*}</u>, Darja Pečko^{1,2}, Muhammad Shahid Arshad^{1,2}, Špela Trafela^{1,2}, Sašo Šturm^{1,2} M. P. Mariana Proenca³, Manuel Vazquez³

¹Jožef Stefan Institute, Department for Nanostructured Materials, Jamova 39, Ljubljana, Slovenia ²Jožef Stefan International Postgraduation School, Ljubljana, Slovenia

³*Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain*

11:50 - 12:10

Influence of current regime on structure and properties of electrodeposited Cu-W alloys <u>Pawel Bacal</u>, T. Ciciszwili, Z. Stojek, M. Donten *The Faculty of Chemistry, University of Warsaw, Poland*



12:10 - 12:30

Electrodeposition of NdFe-based thin films from aqueous solution: the mechanism of Nd and Fe incorporation

Xuan Xu^{1,2*}, Špela Trafela^{1,2}, Spomenka Kobe^{1,2}, Kristina Žužek Rožman^{1,2} ¹Department for Nanostructured Materials, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

²Jožef Stefan International Postgraduate School, Jamova 39, SI-1000 Ljubljana, Slovenia

LUNCH: 12:30 – 14:00

SESSION VI

Chairperson: Nevenka Elezovich (Institute for Multidisciplinary Research University of Belgrade, Belgrade, Serbia)

14:00 - 14:20

Electro-oxidation of formaldehyde using modified Ni electrodes

<u>Špela Trafela^{1,2*}, Kristina</u> Žužek Rožman^{1,2} ¹Department for Nanostructured Materials, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

²Jožef Stefan International Postgraduate School, Jamova 39, SI-1000 Ljubljana, Slovenia 14:20 - 14:40

Electrochemical preparation of iron-based nanofoams via dynamic hydrogen bubble template (DHBT)

Kata Berkesi^{1*}, Evangelos Hristoforou¹, Damion Corrigan²

¹National Technical University of Athens, School of Electrical and Computer Engineering, Laboratory of Electronic Sensors, 15780 Athens, Greece, 9 Herron Polytechniou Str., Zografou Campus

²University of Strathclyde, Faculty of Engineering, Glasgow, G4 ONS, United Kingdom 14:40 - 15:00

Electrodeposition of iron-based nanocomposite coatings

Sundararajan Thirumalai^{1,*}, E. Pellicer², J. Sort², A. L. Greer¹ ¹Department of Materials Science & Metallurgy, University of Cambridge, UK

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PRESENTATION OF CANDIDATURES FOR EDNANO-13 15:00 - 15:20László Peter

15:20-15:40 CLOSING CEREMONY

COFFEE BREAK: 15:40 – 16:00

SATURDAY: 18 MARCH 2017

EXCURSION: Plovdiv and Starosel

Departure at 8:00: Starting point for the excursion - Alexander Nevsky Cathedral, Sofia Arrival at 20:00



16 March 2017 Thursday Session I-IV

Nanostructures where the active component is a single-molecule

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Single molecule devices are of interest for what they reveal about fundamental aspects of electron transport and the interactions of molecules with surfaces. They represent the ultimate level of miniaturization in molecular electronics and are also of potential interest in sensor applications. We use a scanning tunnelling microscope to make and characterize junctions bridged by a single molecule at room temperature. By taking advantage of electrochemistry, we can not only keep the junctions free of oxide and other unwanted contaminants, but also gate them so that they form single molecule transistors. Most work in this field uses passive gold electrodes, but a whole range of interesting effects become accessible when the electrodes are semiconducting or magnetic.

We have created a single-molecule transistor consisting of a 4,4'-bipyridine molecule with Ni electrodes, the latter aligned magnetically via an applied field [1]. The second contact for this device is an electrodeposited Ni film, so this is a genuine electrodeposited nanostructure. The interest in this device lies in the exceptional sensitivity to the gating field (greater than for a similar device with Au electrodes) and in the fact that calculations suggest that the current through the When the central molecule is replaced highly spin-polarized. with 4.4'device is vinylenedipyridine, unexpected new behavior is introduced. Firstly, the measured conductance becomes extremely sensitive to the electrolyte pH as well as the gating potential, so that we have created a unique class of 3-terminal single-molecule sensor, and secondly, we observe unexpected fluctuations in the conductance during a single junction-stretching experiment.

The replacement of one of the metal electrodes by a compound semiconductor presents further opportunities. We have shown recently that single-molecule transport effects can be seen in rectifying GaAs-molecule-metal junctions, and that the choice of molecule also strongly affects the rectification ratio.

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Nanostructure design for photocatalytic water splitting

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With their very high surface-to-volume ratio, the use of nanostructures is highly advantageous for photocatalytic water splitting. But next to their advantage of having a high surface-to-volume ratio, the physical properties of most semiconductors (absorption depth and charge carrier diffusion length) demand the use of one-dimensional nanostructures (e.g. nanowires, nanotubes and three-dimensional nanowire networks) to improve the transport of photogenerated charge carriers to the nanowire surface over the nanowire diameter (~ tens of nm), while maintaining optimal photon absorption over the nanowire length (~ tens of μ m) [1-2].

In my past research and in my new group, the main focus lies on the investigation of these advantages gained by nano-engineering for photocatalytic water splitting considering several different nanostructures. Since templated electrodeposition is a very appropriate technique for designing different shapes of nanostructures with a wide choice of functionalities by materials selection, we use(d) this technique for the design of these different nanostructures for photocatalytic, photoelectrochemical and electrocatalytic water splitting. Among others, these nanostructures include:

- Multisegmented nanowires (ZnO|Ag, TiO₂/Ag) for autonomous photocatalytic water splitting [3-5],
- MoS₂ nanocube structures for electrocatalytic H₂ formation [6], p-Cu₂O nanocubes for photoelectrochemical water splitting [7],
- Mechanically stable and highly interconnected $p-Cu_2O$ and ZnO nanowire networks for photoelectrochemical water splitting [8], and
- Metal Organic Framework (MOF) nanostructures, which are also expected to have many applications in (photo)catalysis [9].

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Electroless deposition of metals on conducting polymer layers

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Metal deposition on conducting polymer (CP) layers is intensively studied in view of the numerous applications of metal particles-modified electrodes, e.g. in the fields of electrocatalysis, conventional and electrochemical As alternative to the electroanalysis sensing. metal electrocrystallization under applied potential or current, CPs offer also the possibility for electroless metal deposition based on their unique intrinsic redox properties. CPs can take different interconvirtable oxidation states and therefore oxidation of pre-reduced CP layers may be coupled with reduction of metal ions present in the electrolyte solution. The coupled redox reaction is selfconfined and depends on the oxidation capacity of the CPs and thus on its amount (or CP layer thickness) as well as on the extent of pre-reduction. This approach is most suitable for deposition of noble metals on CPs and results under specific conditions in finely dispersed metallic nanoparticles with homogeneous distribution on the polymer surface. In a series of papers [1-5] we have studied silver and palladium electroless deposition on polyaniline (PANI) and poly(3,4ethylenedioxythiophene) (PEDOT) layers. The present contribution will give an overview on these studies with focus set on the role of the type of the doping ions used for the synthesis of the CP layers, and concentration and ionic state (cations or anion complexes) of the source for metal reduction.

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Electrodeposited Cu₂O nanowire arrays and networks as photocathode model systems for solar hydrogen production

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In the past decades, research on the synthesis and characterization of semiconductor nanowires has considerably increased, especially for applications in the field of energy conversion, such as for instance in photocatalysis, solar cells, and photoelectrochemical water splitting for hydrogen production [1]. One attractive approach to efficiently absorb sunlight is the use of nanowire architectures since they can offer a large surface area and also permit to reduce the unfavorable ratio of the minority carrier diffusion length over the light absorption depth in comparison to their film counterparts. Among the materials studied as photocathodes for hydrogen generation, Cu_2O is a promising candidate that is earth-abundant, scalable, non-toxic, and compatible with low-cost fabrication processes.

We will present the fabrication and characterization of both highly textured Cu_2O parallel nanowire arrays as well as networks consisting of well-defined interconnected nanowires by electrodeposition in etched ion-track membranes. The membranes are fabricated at GSI by swift heavy ion irradiation of polymer foils, and subsequent chemical etching. Diameter, length, and number density of the nanowires is adjusted by the fabrication parameters. To increase their chemical stability in aqueous electrolyte these photocathodes are conformally coated with a thin amorphous TiO₂ film by atomic layer deposition. The nanowire-based electrodes are employed as model systems to study their photoelectrochemical performance.



Figure 1. (a) Photograph of a Cu2O nanowire network on Au substrate; Scanning electron microscopy images of the nanowire network at (b) low and (c) high magnification.

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Lithium *versus* Sodium Intercalation: Energy Storage beyond Lithium-Ion Batteries

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The interaction of solids having different structure dimensionality with ions via electrochemical intercalation is an original chemical approach that set in 1991 a revolutionary new technology for energy storage by constructing "rocking chair" lithium-ion batteries without using lithium metal as an anode. Nowadays lithium ion batteries are recognized as the most effective technology for energy storage with a variety of applications in different technological sectors. Irrespective of this achievement, lithium ion batteries still have some drawbacks (such as high price, lack of safety and environmental incompatibility) that are not in conformity with modern technological requirements. This necessitates the searching of alternatives to lithium ion batteries. One of possible chemical approaches consists in the replacement of lithium ions with others metal ions while preserving the intercalation mechanism of the battery function. Taking into account the intrinsic properties of the ions such as a standard reduction potential, specific capacity and ionic radius, the most competitive to lithium ions is sodium ions.

This contribution aims to underline how the knowledge on sodium and lithium intercalation can contribute to development of new alkaline ion batteries that go beyond the present lithium-ion batteries. All these features are demonstrated by our recent studies on sodium deficient transition metal oxides, Na_xMO_2 , exhibiting a layered crystal structure. First, the specific ability of $Na_{2/3}Co_{1-2x}Ni_xMn_xO_2$ (x=1/3 and 1/2) to intercalate lithium and sodium ions is presented. The mechanism of Li^+ and Na^+ intercalation into $Na_{2/3}Co_{1-2x}Ni_xMn_xO_2$ is examined by means of powder X-ray diffraction, HR-TEM and EPR of Mn^{4+} . The chemical inertness of electrode materials in organic electrolyte solutions is monitored by XPS analysis. The effect of the particle size distribution and of the electrolyte salt on the intercalation properties of layered oxides is emphasized. Based on the intercalation properties of layered oxides, the fabrication of dual sodium-lithium ion batteries is presented. Finally, the opportunity to store energy by a radical change in the kind of the intercalating ions and of the type of the intercalation compounds is highlighted.

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Determining the Diffusion Mechanism for High Aspect-ratio ZnO Nanowires Electrodeposited into Anodic Aluminum Oxide

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In recent times, ZnO has been extensively studied due to the wide application range which can be employed. ZnO is an n-type semiconductor, exhibits a hexagonal structure, a direct wide band gap of 3.36 eV, high electron mobility, large excitation energy of 60 meV at room temperature, while also presenting an efficient emission in the ultraviolet and visible ranges. One-dimensional structures (nanowires) of this semiconductor are candidates for lasers, photonic devices, chemical sensors, optoelectronic devices, photodetectors and piezoelectric harvesting applications. In general, the improvement of these devices is achieved when ZnO nanowires exhibit high aspectratio [1], highly ordered perpendicular to the substrate [2] and preferential orientation along the *c*-axis of the hexagonal structure of ZnO [3].

The aim of this work is to determine the diffusion mechanism that governs the electrodeposition of ZnO nanowires into AAO templates. In this work, the influence of the ratio of $ZnCl_2$ and H_2O_2

concentrations, reduction potential, and electrodeposition diffusion temperature on the mechanism of ZnO nanowires into AAO aqueous in peroxide solution is studied. Moreover, filling ratio, morphology properties and structural of the nanostructures are studied as a function of the electrodeposition parameters. A good understanding between the electrodeposition parameters, through the diffusion mechanism, the morphological and structural characteristics of the ZnO nanowire arrays is presented for the first time to improve the efficiency of onedimensional ZnO devices. This study opens a new investigation field to be explored due to the great variety of applications for ZnO nanowires.



Figure 1. Diffusion mechanism of ZnO nanowires and top and cross-sectional view of the nanowires.

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Thursday Session II II-3

March 16-18, 2017 – Sofia, Bulgaria

Three-Dimensional Porous Alumina Networks on Cylindrical Aluminum

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We present the formation of a three-dimensional nanostructured network based on ordered porous aluminum oxide with transversal nanopores on a cylindrical aluminum wire. A similar process was already developed in our group to synthesize three-dimensional networks on planar aluminum substrates via pulsed potentiostatic anodization in a sulfuric acid electrolyte [1]. The advantages of the cylindrical geometry of the nanochannels achieved in this work are many, such as the opening of new application fields, for instance in integrated fluidic devices. Moreover, the control of the fabrication parameters in cylindrical substrates is a first step to achieve much more intrincanted functional nanostructures based in this method.





Figure 1: Cross - sectional image of the S180 type sample after a mechanical cut. (a-c) Higher magnification images of limited areas marked by the yellow squares [2]

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Understanding the Fe-Ga deposition in aqueous electrolytes for template based 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. Their ongoing further miniaturization requires low dimensional structures with complex geometries that are only accessible by electrochemical deposition. Extended thin films of Fe80Ga20 were electrochemically obtained from a simple aqueous electrolyte [1]. An induced co-deposition of Fe and Ga takes place while simultaneously huge amounts of oxidic species are formed and incorporated in the deposit [2]. Introducing alternating potential pulses allowed for re-dissolving these oxidic species during the second, more positive potential step. The remaining Fe-Ga alloy layer is homogeneous, dense and exhibits only a negligible oxygen content [1].

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 fill completely the pores and to produce metallic nanowires [3]. At pore diameters below 100 nm the restricted transport properties in the narrow pore geometry inhibit the growth of continuous nanowires. Increasing pH due to strong hydrogen evolution produces large amounts of hydroxides that cannot be completely re-dissolved and removed from the high aspect ratio nanopores therefore leading to discontinuous nanowires with high oxygen contents. By complexing the metal ions in the electrolyte the hydroxide formation and incorporation is almost completely prevented. The resulting alloy nanowires are continuous, dense and do not show a composition gradient along the wire axis [4]. Detailed TEM investigations reveal only minor differences between nanowires prepared by pulse plating or potentiostatic deposition. Both preparation routines produced high quality alloy nanowires which are promising for miniaturized sensor and actuator applications.

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Electrodeposition and of Bi_{1-x}Sb_x nanowire networks and determination of their Seeebeck coefficient

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The unique properties of bismuth antimony $(Bi_{1-x}Sb_x)$ nanostructures and the theoretical predictions on their enhanced thermoelectric efficiency two decades ago^1 triggered the development of a wide variety of growth and characterization methods aiming at measuring the thermoelectrical properties of nanowires. Since then, several groups have studied the properties of $Bi_{1-x}Sb_x$ nanowires and size dependent effects have been highlighted. ²⁻⁴ However, the experimental demonstration of a size dependent thermoelectric efficiency is still challenged by the difficulties encountered to fabricate well-defined nanowire systems and to achieve reliable and stable electrical and thermal contacts. Here we present the fabrication of three dimensional networks of $Bi_{1-x}Sb_x$ nanowires that are assembled and electrically interconnected from four different directions by pulsed electrochemical



Figure 1 SEM image showing an exemplary Bi nanowire network (Size $\approx 100 \text{ x } 100 \text{ } \mu\text{m}$)

deposition in etched ion-track membranes.⁵ The influence of the deposition conditions, and of the additional presence of surfactant in the electrolyte on both wire crystallographic structure and sample homogeneity will be discussed. In addition, we present the experimental evaluation of the Seebeck coefficient measured on both parallel arrays and interconnected networks of $Bi_{1-x}Sb_x$ nanowires embedded in polycarbonate membranes.

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Seebeck coefficient enhancement in electrodeposited $Bi_2Te_{3-y}Se_y$ films with additives and pH variations on the electrochemical bath

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The fabrication of thermoelectric materials, such as chalcogenides (Bi-Te and related compounds) via electrochemical deposition presents many advantages over other fabrication techniques, mainly the low cost, easy scalability to industry and large area coverage. Nevertheless, the thermoelectric properties of chalcogenides are much lower when grown by this method than by other techniques, and there is a lack of understanding the reason behind it. In a previous work, the influence of additives to the electrochemical bath was studied, which improved the morpohology and the Seebeck coefficient of the films [1]. A step further is the combination of these additives with the influence of the pH (that is, the concentration of protons) of the electrochemical bath in the final performance of the films, which should influence the final result given that the reaction that produces the deposit is proton driven. Therefore, both effects have been studied together giving rise to an increase in the Seebeck coefficient from -46 μ V/K when the film is grown with the standard bath composition to around -110 μ V/K with the modified composition and pH.



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Thursday Session III III-3

March 16-18, 2017 – Sofia, Bulgaria

Thursday Session III III-4

Tuning the morphology of tellurium nanostructures by templatefree electrodeposition in ionic liquids : from hollow nanostructures to hair-like nanowires

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Electrodeposition of nanowires is usually performed in a porous template and involves multiples fabrication steps, like the preparation of the template and its removal. A single step template-free electrodeposition would in some cases be more convenient, for example to synthesize core@shell

structures. It has been shown in literature that ionic liquids, in addition to have high electrochemical and thermal stabilities, can act as capping agents allowing the formation of nanostructures without using a template [1].

We will present here the template-free electrodeposition of Te nanostructures in a piperidinium ionic liquid. A systematic study of the influence of synthesis parameters revealed that the deposits morphology mainly depends on mass transport conditions and Te(IV) speciation. diffusional Under control, nanowires are deposited (Figure a), whereas by applying high overpotential values and then severe mass



transport conditions, hollow nanostructures are formed due to a limitation by species supply (Figure b) [2]. The electrolyte composition determines the Te(IV) speciation that also strongly influences the morphology of the nanostructures. Specifically, the addition of a small amount of bromide ions in the electrolyte allows to synthesize 70 μ m long hair-like nanowires with a mean diameter of 50 nm (Figure c) [3]. High Resolution Transmission Electron Microscopy analyses show that the nanostructures are single crystalline and grow along the *c*-axis, with a smooth interface and no external surface layer (Figure d).

Examples of core@shell nanostructures that could present interesting properties in the field of thermoelectrics will also be presented, elaborated by electrodeposition of a shell on the Te nanowires.

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Shape-Controlled Electroless Plating of Silver Nano-Platelet Films

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To facilitate the implementation of nanomaterials, there is a strong need for innovation beyond cleanroom processing and for flexible, simple and robust synthetic routes to nanomaterial fabrication. Here we demonstrate how the wet-chemical method of electroless plating can be tuned to produce deposited silver films composed of plate-like, shape-controlled nanoparticles. Due to the wide functionality range of Ag nanostructures and the shape-sensitivity of many of their properties,¹ we deem this approach as a highly productive route toward materials for e.g. catalytic and plasmonic applications.



Figure 1. SEM images of Ag films composed of (a) solid platelets, (b) micron-sized, porous platelets, and (c) micron-sized platelets with dendritic, wiry edges.

Following the strategy outlined in a previous study,² planar growth was induced by tuning the underlying reduction and oxidation reactions, resulting in the suppression of 3D nucleation and the development of 2D particle shapes. This control enables Ag platelet deposition over a wide range of experimental conditions, including the presence of anions (e.g. sulfate) and surfactants (e.g. CTAB), as well as the absence or presence of seed particles. Depending on the conditions, synthesis varying product morphologies can be obtained, ranging from relatively dense arrangements of platelets of ca. 100 nm edge length, to open-porous films composed of micron-sized, high-aspect-ratio plates exhibiting a dendritic structure (Fig. 1).

The outlined approach is fast (< 1 h reaction time), flexible regarding the substrate, does not require complex instrumentation, uses only standard chemicals, and is readily scalable.

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Preparation and characterization of TiO₂ nanotube arrays with enhanced photoelectrochemical performance

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Highly ordered TiO_2 nanotube arrays (TNTA) are proved to be very efficient as physical and chemical nanodevices due to their valuable high surface area structure, excellent photocatalytic, optical and electrical properties [1]. TNTA show enhanced photoelectrochemical performance and better catalytic activity when compared to sol-gel particulate TiO_2 layers. TiO_2 nanotubes are formed by anodic oxidation of the titanium substrate (a simple, low-cost and recyclable method for preparation) in glycerol solutions and subsequent annealling at 500°C for crystallization.

However, in sunlight TNTA absorption range is limited to ultraviolet (UV) spectrum only, due to wide band gap (3.2 eV). This, along with the fast recombination rate of photo-generated electron-hole pairs

still restricts their practical application [2]. One of the strategies to overcome these problems is doping with non-metal elements, such as boron and nitrogen [3]. First, the titanium sheet is anodized and subsequent titania is electrochemically treated in an electrolyte, containing boric acid. The as-prepared B-TNTA are annealed in N₂ atmosphere at 500°C for 2 hours to produce B,N-TNTA. The samples are characterized by: SEM, AFM, XRD, XPS and UV-Vis diffusion reflectance spectroscopy. The B,N-TNTA consist of uniform and well aligned nanotubes with an average inner diameter of 80-100 nm and a length not exceeding 1 µm.

The photocurrent response measurements of the TNTA, N-doped and B,N-co-doped samples are performed under UV and visible



LSV curves of undoped and doped TNTA anodes under UV light

(Vis) light irradiation. In order to further study the doping effect, the photocatalytic activity of the samples is evaluated by the degradation of methyl orange (MO) under UV and Vis light irradiation. The obtained results show that the B,N-doping leads to a remarkable photocurrent enhancement and increased removal rate of MO both under UV and Vis light illumination.

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12th INTERNATIONAL WORKSHOP ON ELECTRODEPOSITED NANOSTRUCTURES

March 16-18, 2017 – Sofia, Bulgaria



17 March 2017 Friday Session IV-VI

Glow discharge – time-of-flight mass spectrometric composition depth profile study of electrodeposited Ni-Cu/Cu multilayers

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Electrodeposited multilayers and compositionally modulated alloys are in the focus of interest for their mechanical, magnetic and corrosion properties. The result of the deposition process and the related layer structure can be visualized with the help of Transmission Electron Microscopic (TEM) images. However, a TEM study requires a long sample preparation time; hence, sputtering-based composition depth profile analysis methods can rather be applied as a routine check of the layer structure with nanometric resolution in a large depth scale. Glow Discharge – Time-of-Flight Mass Spectrometry (GD-ToFMS) is a relatively new technique that combines the feature of the well-known glow discharge sputtering method with a high-resolution mass spectrometric analysis. This is the first time when electrodeposited multilayers are studied with this technique.

Samples were deposited onto a pre-coated Si wafer and with a solution containing nickel sulfate, nickel acetate, copper sulfate, sodium citrate and sodium chloride [1]. The deposition of the Cu layers was regulated in potentiostatic mode, while the galvanostatic mode was applied for the deposition of the Ni-Cu layer and its composition was adjusted with the deposition current density. The typical layer structure obtained follows: was as Si/Cr(5)/Cu(20)//Cu(20)/Ni-Cu1(80)/Cu(80)/Ni-Cu2(80)/Cu(80)/Ni-Cu3(80)/Cu(20) where the numbers in parenthesis refer to the layer thickness in nanometers and those next to the Ni-Cu layer refer to different layer compositions.

It was found that the resolution of the GD-ToFMS method was sufficient both to resolve the layer structure and to distinguish the Ni-Cu layers of different composition. A new observation was that the presence of some minority components (impurities like C or Na) is observed mainly in the Cu layer, while alloying elements (Co and Fe) accumulate in the Ni layer. The impurity accumulation in the Cu layer may significantly influence the transport properties of such electrodeposited multilayers.

Qualitative composition depth profile 1,0E+09 1,0E+08 1,0E+07 ntensity / cps 1.0E+06 1,0E+05 1.0E+04 1,0E+03 Amp-par WWW mmanhah 1.0E+02 0 50 100 150 sputtering time / s

Reference

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Copper and copper oxide nanoparticles: A plasmonic perspective

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Copper nanoparticles (NPs) represent an inexpensive alternative to the more expensive gold and silver plasmonic NPs, particularly in systems that may require large plasmonic surface layers, as in plasmonic solar cells and metal-enhanced fluorescence, as well as in (photo)catalysis, conductive inks and antibacterial agents. However, Cu NPs are sensitive to oxidation and corrosion processes, which may preclude many of these applications.

Here we investigate the possibility of using localized surface plasmon resonance (LSPR) measurements for studying the oxidation kinetics of Cu NPs. The NPs were deposited using a chemical deposition method on glass and FTO substrates [1], and their oxidation kinetics were studied by LSPR spectroscopy during their thermal annealing in air at intermediate temperatures (100-170°C). The NP structure at different stages of the oxidation was evaluated by SEM and TEM, while compositional analysis was performed using electrochemistry, X-ray photoelectron spectroscopy (XPS) and grazing-incidence X-ray diffraction (GIXRD).

Making use of the sensitivity of the optical response of Cu NPs to dielectric changes, the Cu-to-Cu₂O NP oxidation was studied by in-situ LSPR spectroscopy to determine kinetic parameters of the nanoscale solid-state oxidation process, and to understand the optical evolution of the system in plasmonic terms. Under the chosen oxidative conditions, Cu NPs develop an initial Cu₂O layer that eventually leads to hollow Cu₂O NPs via the nano Kirkendall effect (NKE). The oxidation progress is characterized by an initial increase of the LSPR extinction intensity followed by a gradual decrease, as well as a continuous red-shift of the LSPR band wavelength.

A general kinetic model was developed and combined with Mie scattering theory in order to theoretically describe the optical evolution of the system upon oxidation, requiring consideration of the observed nano Kirkendall effect [2].

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Friday Session IV IV-3

March 16-18, 2017 – Sofia, Bulgaria

Tuning the magnetic properties of multisegmented Ni/Cu electrodeposited nanowires with controllable Ni lengths

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The fabrication of segmented Ni/Cu nanowires (NWs), with structural and magnetic properties, will be tunable presented. A potentiostatic electrodeposition method with a electrolytic bath has been used to fabricate single multisegmented Ni/Cu NWs inside a highly hexagonally ordered anodic nanoporous alumina membrane, with diameters of 50 nm and Ni segment lengths (L_{Ni}) tuned from 10 nm up to 140 nm. The x-ray diffraction results evidenced a strong dependence of the Ni NWs crystallographic facecentered-cubic (fcc) texture along the [220] direction on the aspect ratio of the NWs. 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. Micromagnetic simulations, together with the experimental results, showed a dominant antiferromagnetic coupling between Ni segments along the wire length for small low aspect-ratio magnetic segments. When increasing the Ni segments' length, the magnetic interactions between these along the wire became stronger, favouring a ferromagnetic coupling. The Curie temperature of the NWs was also found to strongly depend on the Ni magnetic segment length [1]. Particularly the Curie temperature was found to be reduced 75K for the 20 nm Ni segments, following the finite-size scaling relation with ξ_0 =8.1Å and γ =0.48 [1, 2]. 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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Electrodeposition of morphological selected nano metal deposits and Pd films from ionic liquids

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Micro- and nanostructered surfaces are of growing interest for technological applications [1]. For nanoparticles size and shape are important factors in determining their physical properties [2-3]. In the last years, nanostructered surfaces and nanoparticles with specific shapes have been prepared, such as nanotubes, nanowires and nanoflowers [4-7].

Electrochemical deposition, as well as various chemical techniques is currently in use for the preparation of nanocrystalline deposits or metal nanoparticles of different geometries and shapes. Electrochemical processing techniques are promising because of the control of the electrocrystallization process (mass, shape, morphology or thickness of the deposits) by adjusting the parameter current density, metal concentration, hydrodynamic and temperature [1].

Ionic liquids (synonym: room-temperature molten salts) are a relatively new type of electrolytes. Their physicochemical properties are similar to high temperature molten salts, but the practical aspects of their handling are quite different (for instance, liquid at or near room-temperature, low corrosivity, composed of either inorganic/organic or organic/organic anions and cations). Metal electrodeposition from ionic liquid based electrolytes requires a high overpotential. This is mainly due to the high viscosity, low conductivity of the ionic liquids and the strong interactions among the ionic components in the ionic liquid and at the interface substrate/electrolyte. It has been shown that moisture and water stable ionic liquids like 1-butyl-3-methylimidazolium chloride tetrafluoroborate [8-9], can successfully be used as solvents for metal electrodeposition.

The present paper shows some examples of preparing morphologically interesting nano- and microstructered metal deposits by galvanostatic deposition from ionic liquids at different current modes and under the influence of organic additives.

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Electrodeposition of Co nanowires from deep eutectic solvents (DESs) and analogous

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Magnetic nanostructures have attracted the attention because of the unique properties observed at the nanoscale level e.g. high saturation field, anisotropy [1]. These materials find a wide range of application from information recording and storage to microelectromechanical systems (MEMS).

In this work, deep eutectic solvent (DES) and ionic liquids analogous based on ethylene glycol are considered as alternative to water-based ones [2]. In the latter, the dependence of deposits microstructure on bath composition (e.g. pH) is already studied [3, 4]. Considering a non-aqueous system, the concept of pH is limited; moreover, the lack of water minimizes the hydrogen evolution at the cathode [2]. In this study, deposits microstructure and morphology are studied varying operational parameters and solution composition considering non-aqueous systems. Nanowires are fabricated using a 100 nm diameter inorganic membrane.

Electrochemical characterization of the considered electrolytes is performed by means of cyclic voltammetry. Subsequently, potentiostatic electrodepositions are carried at low temperature e.g. 40 °C. XRD analysis is performed to assess microstructure for both film and nanowires. Cross section of both film and nanowires is observed by means of scanning electron microscopy (SEM).

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Electrodeposition of cobalt-ruthenium alloys from acidic chloride ions containing baths

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The article presents results of tests on potentiostatic electrodeposition of ruthenium and Co-Ru alloys. The tests applying the method of cyclic voltammetry with the use of gold disk electrode (RDE) allowed to define a potentials range in which it is possible to obtain ruthenium and its alloys with cobalt from acid chloride electrolytes.

The influence of electrodeposition parameters and the electrolyte composition on the composition, morphology and structure of the obtained deposits was determined. Co-Ru alloys underwent XRD tests, an analysis with the XRF method and observations using scanning electron microscopy (SEM).

Friday Session V V-2

March 16-18, 2017 – Sofia, Bulgaria

Tailoring the magnetization direction in electrodeposited Fe-Pd and Co-Pt nanowires

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Nanowires (NWs) have unique potential when talking about their applications either in magnetic storage and magnetic-based nanodevices. Due to the constrains on the nanolevel the magnetization can follow unique directions governed by the nanostructure crystal structure, size and shape. In order to investigate different anisotropy contributions the magnetization distribution and switching study was perfomed on fcc Fe50Pd50-based nanowires (NWs) and Co-rich hcp Co80Pt20 nanowires. For the in-field MFM measurements on electoplated Fe-Pd and Co-Pt NWs a homemade stage was used. The maximum external field applied to the NWs was applied via permanent magnet with the maximum applied etrean field (Hmax~240 kA/m) which's direction was varied. Using electrodeposition into anodic aluminium oxide membranes fcc Fe48Pd52 and hcp Co80Pt20 NWs with diameters of ≈ 200 nm and lengths of ≈ 3.5 µm were synthesised. Magnetic force microscopy on a single Fe-Pd NW revealed single-domain behaviour with the easy axis of magnetization along the long axis of the NW. The magnetization-switching behaviour of a single Fe-Pd NW studied with MFM suggested a square-shaped magnetization curve (M/Ms=1) with HC \approx 3.2 kA/m. By using in-field MFM technique, the effect of dipolar interactions in Fe-Pd array of NWs still embedded in the AAO was examined and found that the dipolar interactions greatly reduce the remanence and the switching-field distribution of the Fe-Pd NW array. In the case of the Co-Pt NWs the texturing of the direction [100] was observed that suggests the uniaxial anisotropy perpendicular to NW long axis. The subsequent magnetic results obtained via "bulk" methodes VSM and first order reversal curves (FORC), allowed us to conclude that Co-Pt NWs with hcp crystal structure had a uniaxial anisotropy perpendicular to NW long axis. This was found further to result in a unique periodic domain structure observed with MFM. By using an adopted equation to calculate the period of the stripes or the domain width for the nanowires we estimated a domain width of Wcal ≈ 250 nm to minimize the total energy, which is in excellent agreement with the present observations. Such a type of domain pattern is the state with the lowest energy that can be applicable in the newest version of race track memory devices with perpendicular anisotropy.

Influence of current regime on structure and properties of electrodeposited Cu-W alloys

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Tungsten cannot be electrodeposited from aqueous solutions alone, although it is possible to obtain its alloys with the elements from the iron triad. This phenomenon, called by Brenner ,,the induced codeposition" [1,2], was recently extended to copper and silver [3,4]. So far, it was possible to electrodeposit good-quality, compact and adhesive layers of copper – tungsten alloys from citrate baths under direct current regime [5]. The maximal content of tungsten was ca. 10 $\%_{at}$ and the alloys had a complex internal structure built of two major phases. Those deposits were composed of pure copper nanocrystals immersed in a tungsten-rich nanocrystalline/amorphous phase. This segregation could be caused by the fact that tungsten and copper do not form thermodynamically stable binary forms. However, limited miscibility of Cu and W was observed in the electrodeposited Cu-W alloys.

To reduce the number or copper excretions in the alloys described above, authors decided to perform electrodeposition of Cu-W under pulsed-current conditions. This approach allowed us to increase both: CE and tungsten content compared to results obtained under direct-current regime. It has been found that an increase in tungsten content was strongly related to CE of the process. The alloy exhibited the same light orange color and a satin shine. Authors were able to obtain even dozen-micrometer thick deposits. This fact in combination with the high tungsten content (up to $20\%_{at}$), unique internal structure and good appearance is hopeful in terms of industrial usage and further development of this nanostructured coverage.

The obtained results of pulsed electrodeposition of Cu-W alloys are compared with those for directcurrent regime. They are presented with emphasis on materials internal structure and the correlation between content of tungsten in the alloys and conditions of the deposition process.

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Friday Session V V-4

March 16-18, 2017 – Sofia, Bulgaria

Electrodeposition of NdFe-based thin films from aqueous solution: the mechanism of Nd and Fe incorporation

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Figure 1. The cross-section with EDXS maps of Zn-coated Nd-Fe-based thin film

Nd-Fe-based thin films modified with nitrogen i.e NdFe₁₂N_x are of great interest because of their intrinsic excellent magnetic properties [1]. Electrodeposition of NdFe-based thin films from aqueous solutions is very attractive because of the lower cost, higher deposition rate and easier operation, compared to non-aqueous solutions but possesses a number of challenges. Since Nd^{3+} can be hydrolyzed to $Nd(OH)_3$ because of the H_2 evolution reaction, resulting from the very negative deposition potential needed for Nd³⁺, while metallic Nd reacts with O_2/H_2O instantly to form $NdO_x/Nd(OH)_x$. Whether Nd is deposited in the metallic form or as oxides/hydroxides is still not clear from the literature [2]. In this study, Nd and Fe were co-deposited as reported [2] using galvanostatic mode with one layer of Zn protective coating onto the copper substrate from aqueous chloride solution containing glycine as the complexing regent. The deposits composition and

morphology were investigated by scanning electron microscope (SEM) coupled with energy dispersive Xray spectroscope (EDXS). NdFe-based deposits containing Nd 2~7 at.% could be tailored by changing the applied current and glycine concentration. The as-deposited thin film without Zn coating appeared to be amorphous with soft ferro-magnetic response. The cross-section of the Zn-coated NdFe deposit was prepared by focused ion beam (FIB) in order to investigate the elements distribution vertically in the thin film. Nd-rich layer with the thickness of around 2 µm was formed at the beginning of deposition. Oxygen was found throughout the whole film deposit, reportedly most probably coming from NdFe(OH)_x or NdFeO_x [3]. However, if these nonconductive metal oxides/hydroxides were formed during deposition, they would probably hinder the onward deposition, which was not the case. It is also unreasonable to believe that metallic Nd was oxidized after deposition according to the EDXS maps. Therefore, X-ray photoelectron spectroscopy will be done to reveal the metals oxidation states in the coated film.

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Electro-oxidation of formaldehyde using modified Ni electrodes

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In this study we used KOH-modified Ni electrodes for the electro-oxidation of formaldehyde (HCHO), which are promising to be used as an effective electrochemical receptor element. Ni "films" were deposited on Au substrates by the electro-deposition from acidic and neutral NiSO₄-based solutions with subsequent modification in 1 M KOH. From the SEM results we found out that pH of Ni^{2+} solution affects the morphology of the deposited films. Under acidic conditions homogeneous Ni film was formed, but under neutral conditions porous Ni film was deposited. The modification step with KOH is very important for the further investigations of HCHO oxidation, because NiO(OH)/Ni(OH)₂ redox couple exhibits high catalytic activity towards HCHO.

The electro-catalytic activity of modified Ni-based electrodes (Ni-OOH) for formaldehyde detection in alkaline media was investigated via a series of electrochemical measurements. The potential range for modification in KOH has to be chosen in the region where oxygen does not form (the maximum potential 0.6V), because molecular oxygen can be adsorbed on the electrode and inhibits further oxidation of HCHO [1].

Experimental results show that the electrode displays a remarked electro-catalytic activity for the oxidation of HCHO and exhibits a linear relationship in a concentration range from 1 mM to 1 M. An oxidation peak was obtained at potentials around 0.5 V vs. Ag/AgCl for concentrations 1 mM - 0.1 M and around 0.8 V vs. Ag/AgCl for concentrations above 0.1 M. Results showed that the reaction of the electro-oxidation is activation controlled and most probably proceeds by a chemical reaction with NiO(OH) as shown on Scheme 1 [2]. The experimental data further reveal that porous Ni film exhibits a higher sensitivity (approximately 7x higher) compared to the homogeneous Ni electrode, because the slope of the curve current signals vs. concentrations reached higher value. We believe this is due to the more surface active sites and connected higher amounts of adsorbed – OOH groups that promote the electron transfer between receptor elements and HCHO molecules. These advantages of porous Ni film make it promising for providing a low cost and simple method in real samples.

NiO(OH) + formaldehyde \longrightarrow oxidised formaldehyde + Ni(OH)₂

Scheme 1: Formaldehyde oxidation on modified Ni electrodes

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Electrochemical preparation of iron-based nanofoams via dynamic hydrogen bubble template (DHBT)

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The Dynamic Hydrogen Bubble Template (DHBT) is an excellent method for the fabrication of macrostructures with nanoporous side walls [1,2]. The technique has been named from the phenomena when a series of hydrogen-bubbles generated on the surface of the substrate act like a dynamic negative template. In Figure 1 the theoretical approach of the technique is demonstrated. Fig 1-left draw represents the hydrogen-evolution takes place on the surface where is no metal/metal-oxide deposition. Fig 1-right picture shows the SEM-image of copper nanofoams prepared by DHBT [4].



Figure 1. left: Simplified description of DHBT generated metal/metal-based foams [3], right: Honeycomb-like Cu-deposit structure made by DHBT [4].

Iron-based semiconductors nanonstructures have great attention regarding different applications in microelectronics and transducer industry due to their exellent magnetic properties. Iron-based nanofoams have been prepared via DHBT. Several bath compositon, bath temperature, additives, deposition time have been studied. Cyclic voltammetric studies have been made to determine electrochemical behaviour on the substrate/deposit interface. Structural and morphological properties have been studied by Scanning Electronmicroscope (SEM) and X-ray diffraction (XRD).

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Electrodeposition of iron-based nanocomposite coatings

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Abstract:

Due to their practical advantages over vapour-based techniques, such as fast deposition rates, nonrequirement for ultra-high vacuum, low cost, and ease of coating complexshapes, electrodepositionbased techniques are attractive for the development of nanocomposite coatings[1]. Among the nanocomposites prepared electrodeposition, titanium various types of by nitride-based electrodeposited nanocomposites have received considerable attention in recent years. Examples include Ni-TiN[2] and NiFe-TiN[3]. In this work, we report preliminary results on coelectrodeposition of novel Fe-TiNnanocomposites using an iron-sulphate-based bath and TiN nanoparticles. The stability of the TiN nanoparticles in the electrolytic bath was determined with help of zeta potential measurements. Coatings were characterized by scanning electron microscopy to get insights about the incorporation of TiN nanoparticles in the iron matrix. Effects of surfactant addition, current density, pulse- and reverse-pulse-plating parameters on the incorporation of nanoparticles are studied. Pulse-plating improved the incorporation of nanoparticles in the coatings.

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12th INTERNATIONAL WORKSHOP ON ELECTRODEPOSITED NANOSTRUCTURES

March 16-18, 2017 – Sofia, Bulgaria



12th INTERNATIONAL WORKSHOP ON ELECTRODEPOSITED NANOSTRUCTURES

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Thursday, 16 March Poster session

Electrodeposited NiSn coating as the catalysts for alkaline water electrolysis

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(a) SLT for the HER; (b) SLT for the OER;
(c) SLT for the average cell voltage (U_{av}).

NiSn based coatings alloys were electrodeposited onto Ni 40 mesh substrate tested as cathodes and anodes for the and alkaline water electrolysis application in 30 wt.% KOH at 80°C. The "service life test" performed for the hydrogen (SLT) was evolution reaction (HER), as well as for the oxygen evolution reaction (OER), and compared to that recorded for the Ni coating for both reactions. The morphology and chemical compositions of the NiSn and Ni were investigated coatings by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), while the surface composition was investigated by XPS before and after the SLT for both reactions, respectively.

By measuring the potential at the current density of 0.3 A cm⁻² it was shown that during the SLT the overall cell voltage decreased for about 26 mV when the NiSn alloy coating catalyst was applied. Thus, the cell voltage decreased about 150 mV and 26 mV during the SLT, for the Ni electrode and the NiSn electrode, respectively. Hence, the cell voltage saving with the NiSn electrodes amounts to about 435 mV before the SLT and about 304 mV after the SLT. These results make NiSn coating promissing for alkaline water electrolysis application.

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Comparative analysis of chemically and electrochemically produced silver powders of nanostructural characteristics

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Silver powder particles of nanostructured characteristics were produced by the galvanostatic regime of electrolysis and compared with those obtained by chemical reduction with hydrazine. Morphology of all types of powder particles was examined by the technique of scanning electron microscopy (SEM), while crystallographic characteristics were examined by the X-ray diffraction (XRD) analysis of the obtained particles. Morphology of the electrochemically produced powder particles strongly depended on the type of used electrolyte. The irregular crystals and the needlelike dendrites were predominately formed from the nitrate (acid) electrolyte. On the other hand, the 3D pine-like dendrites very similar to Cu dendrites [1] were formed by the electrodeposition from the ammonium (alcali) electrolyte. Simultaneously, the particles of spherical shape were formed by chemical reduction with hydrazine. The difference in morphology of electrochemically produced Ag powders can be explained by different rate of the electrochemical process by which they are formed. Namely, the ammonium electrolyte belongs to the group of the complex electrolyte and formation of this complex lowers the exchange current density for Ag causing a transfer of Ag from the group of the normal metals (metals with the high values of the exchange current density) to the group of the intermediate metals (metals with the medium values of the exchange current density). Irrespective of the way of preparation of Ag powder, Ag crystallites in all types of powder particles were predominantly oriented in the (111) plane. Formation of powder particles of the different shape with the strong (111) preferred orientation was discussed and explained by the consideration of the general characteristics of the growth of a crystal in the crystallization and electrocrystallization processes. Analogy between these two types of processes was made and discussed.

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The morphology of Zn-Mn electrodeposits obtained from choline chloride-urea deep eutectic solvent

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During the last decade, choline chloride-based deep eutectic solvents (DES) have been successfully used for electrodeposition of different metals (Cr, Mn, Cu, Ag, Fe, Zn) and alloys (Zn-Cr, Zn-Sn, Zn-Ni, Zn-Mn, Ni-Co) on different substrates, producing films with characteristics that are completely different from those obtained from aqueous electrolytes [1].

The Zn-Mn alloys electrodeposited from DES are expected to be superior in corrosion resistance compared to those from aqueous solutions. However, the literature on the electrodeposition of Zn-Mn alloy from DES is very scarce, and the influence of various deposition parameters on the coating morphology has not been investigated in detail. Therefore, the aim of this work was to analyze the appearance and morphology of the Zn-Mn coatings electrodeposited from DES, by using scanning electron microscopy and atomic force microscopy.

From the comparison of the SEM and AFM micrographs of the coatings obtained in aqueous solution and DES under the identical conditions, it may be concluded that the deposition from DES enables the formation of the coatings with higher Mn percent, retaining the morphology characteristic for the coatings obtained at low current densities, i.e. smooth and compact, with closely packed platelets.



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Effects of selected additives by the electrodeposition of Pd films from non-aqueous solutions

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This work is part of the joint research project ,,development of new electroplating processes from ionic liquids" which was recently starting in Germany. In a suboperation, the effects of selected additives on the electrodeposition of Pd films from non-aqueuos solutions should be investigated by our working group. Prosperous use of organic additives by the electrodeposition of Pd films from non-aqueous solutions was recently reported by Böck et al. [1].

The investigation of the influence of different organic additives, current modes and hydrodynamic conditions on the morphology of Pd crystallites in the beginning of Pd film formation was in the focus of the experiments. In a first cut, the possibly influence of the selected additives on the deposition potential (overpotential) was characterized by different voltammetric experiments. The next step involved several electrodeposition experiments by variing the additive compound, deposition time and current density.

In order to determine the surface morphology and thickness of the electrodeposited Pd crystallites/Pd films, a high resolution scanning electron microscope and an energy dispersive X-ray fluorescense spectroscope were used.

The first experimental results show that the surface morphology of the Pd films could be remarkably affected by either addition of additive or by applying diffent current modes. These results indicate that it is possible to optimise the quality of Pd deposits from non-aqueous solutions by addition of an appropriate additive.

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MOF and metal oxide nanostructures for photocatalytic water splitting

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With their very high surface-to-volume ratio, the use of nanostructures is highly advantageous for photocatalytic water splitting. But next to their advantage of having a high surface-to-volume ratio, the physical properties of most semiconductors (absorption depth and charge carrier diffusion length) demand the use of one-dimensional nanostructures (e.g. nanowires, nanotubes and three-dimensional nanowire networks) to improve the transport of photogenerated charge carriers to the nanowire surface over the nanowire diameter (~ tens of nm), while maintaining optimal photon absorption over the nanowire length (~ tens of μ m) [1-2].

On this poster, we will present the preliminary results and plans for our future research on:

The design of Metal Organic Framework (MOF) nanostructures via electrochemical oxidation, and their modification for photocatalytic water splitting [3].

Photocatalytic metal oxide nanostructures made via templated electrodeposition in i.e. interconnected anodized aluminium oxide (AAO) templates [4].

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Increasing the Compositional Complexity of Nanotubes and Nanotube Networks

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Porous, nanostructured metals display an emerging central class of functional materials for electrochemical applications.¹ Using electrodeposition or electroless plating in conjunction with ion track etched membranes provides access to tailored nano-architectures of this kind, including nanotubes, nanowires, and networks composed of such building blocks.²

In this contribution, we show how simple redox chemistry can be used to modify and adjust the composition of such materials. For instance, thermal oxidation can be applied to transform Cu nanotube networks to oxide derivatives (Fig. 1 a), which can adopt a porous core-shell architecture due to the nanoscale Kirkendall effect (Fig. 1 b). Electroless plating can be used to homogeneously coat metal nano-networks with a thin layer of a second metal, e.g. Ni for corrosion protection or the introduction of catalytic activity (Fig. 1 c). Adjusting the metals employed in electroless seeding and plating reactions allows to realize bior multimetallic nanotubes (Fig. 1 d).^{3,4} Such materials can be designed to possess multiple functionalities and synergetic behavior.^{3,4}

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Figure 1. (a) SEM image of a free-standing network film composed of multilayered Cu oxide nanotubes, and (b) the TEM cross section of the corresponding tube walls. (c) TEM image of a nanocrystalline Cu tube wall covered with a thin, semi-amorphous Ni layer. (d) Cyclic voltammogram of Au-Pt nanotubes (scan rate: 20 mV s⁻¹, electrolyte: 0.1 M NaOH).

Electrochemical deposition of CoNi-PPy composite structures by changing Co concentration

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CoNi-PPy composite structures were electrochemically grown in two steps. Firstly, PPy layer with thickness of 2 μ m was electropolimerized. Then CoNi particles were electrodeposited from solutions containg NiSO₄ (0.3 M) and CoSO₄ (0-0.5 M). Structural analysis was made by a Fourier transformed infrared (FTIR) spectrometer and a scanning electron microscope (SEM). The chemical composition was determined by an energy dispersive X-ray (EDX) spectrometer. For the samples, the peaks belonging to C, N, O, Co and Ni were detected. The white colored particles seen on Fig.1 (a-c) are (Co)Ni particles (by EDX). As the Co concentration in the solution incraeses, the distance between the particles inreases and the size of the particles gets bigger. M-H curves of the samples were measured by a vibrating sample magnetometer (VSM) and given in Fig. 1 (d-f). The magnetization value increases and the saturation field shifts to high magnetic fields depending on increment Co concentration in the solution and hence Co content of the samples.



Figure 1. SEM images (a-c) and M-H curves (d-f) of CoNi-PPy composite structures depeding on Co concentration

Poster Session P-8

Structural and optical properties of electrodeposited NiO thin films

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Nickel oxide (NiO) thin films were potentiostatically electrodeposited on ITO substrates from a solution containing nickel nitrate, and their thicknesses were varied from 100 to 500 nm. The solvents for the solution were ultrapure water, ethanol and blend of them at different ratios. According to the recorded current-time transients, as the ethanol content increases the cathodic current decreases (Fig. 1a). The structural analysis was done by a Fourier transform infrared (FT-IR) spectrometer. For all films, the characteristic transmittance peaks of Ni₂O and Ni₃O appeared. The morphology of the films was studied by a scanning electron microscope (SEM) and the chemical composition was analyzed by an energy dispersive X-ray (EDX) spectrometer. The peaks belonging to Ni and O were obtained. The optical properties were examined by an ultraviolet-visible (UV-VIS) spectroscope and a photometer for light absorption (transmission). UV spectra showed that the absorbance value increases as the thickness increases for the films produced from the solution containing ethanol.



Figure 1. (a) current-time transients, (b) transmittance variation (c-e) transmittance results.

Poster Session P-9

March 16-18, 2017 – Sofia, Bulgaria

EDNANO12

Electron microscopy analysis and magnetic characterization of Ni-Co/Cu multilayered nanowires grown in AAO membranes

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Ni-Co/Cu multilayered nanowires were fabricated by template-assisted nanowire growth in anodized aluminium oxid (AAO) membrane from an optimized aqueous electrolyte by using two-pulse The segmented magnetic/ non-magnetic plating. nanowire structure was achieved during growth length of the nanowires. along the The electrodeposition parameters were set to obtain equal thicknesses of both kinds of layer with a repetition period of 10 nm. Structural characterization of the nanowires was carried out using SEM, TEM, HRTEM, SAED and EELS techniques.

These techniques yielded results confirming the multilayered structure of the nanowires. Figure 1 shows the TEM image of a single multilayered Ni-Co/Cu nanowire which was released from the AAO membrane by dissolving the template. An alternating dark and light layering sequence can be observed at the edges of the wire, both layer types



Fig. 1 TEM image of a Ni-Co/Cu multilayered single nanowire (Inset: SAED pattern of the red zone marked on the TEM image).

having an approximate thickness of 5 nm. The diffraction pattern was measured by using SAED (see inset in Fig. 1) from the red rectangular area of the nanowire. After indexing the pattern, we found that both the magnetic and non-magnetic layers have an fcc structure. Furthermore, from the magnetic hysteresis loops measured on the nanowire array within the template in a VSM, with the magnetic field being parallel or perpendicular to the wire growth direction, we found a coercivity value of 118 Oe or 89 Oe, respectively



Morphology of the self-organized copper-antimony electrodeposited alloys

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Comparative investigations of the surface morphology of electrodeposited copper- antimony alloys with spatio-temporal structures onto their surface and cross-sections are performed by means of optical, scanning-electron and atomic-force microscopy.

The morphology of the different phases forming the heterogeneous structures is quite different and they are well distinguishable in the SEM measurements with a different technique (Fig 1). The coatings with periodical spatio-temporal structures are multilayered with very small thickness of the separate sublayers and in the SEM images the areas of the different phases (dark and light areas) are well visible.



Figure 1. Scanning – electron image of the electrodeposited copper-antimony alloys

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Spatio-temporal structures of electrodeposited indium based alloys

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The pattern formation observed on solid electrodes during electrodeposition of some indium alloys under well controlled electrochemical conditions are attractive and rare systems in which the pattern are constituted of metals. The experimental conditions of those systems can be reversibly and quickly changed by altering external parameters, differently from chemical parameters. That's why these systems could be used as a prototype models to facilitate a classification of the phenomena of self-organization. Also, the pattern and structure formation phenomena indicate the possible existence of new unknown properties of the alloy coatings what is a general conclusion from the investigations of self-organization phenomena. In this research indium based alloys were electrodeposited and obtained spatio-temporal structures were investigated The spatio-temporal structures exist in the different scales, so the different magnification and technique could elucidate the phenomena of scaling in the case of pattern formation. For this purpose, measurements using techniques such as Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) under well-defined conditions were realized. The level of self-similarity of the pattern formation at the solid surfaces was investigated. Different types of scaling in the three different indium alloys -Pd-In, Au-In and In-Co were observed. The establishments of appropriate areas with expected selfsimilarities part of the deposited samples open the possibilities to discuss mechanism of the pattern formation from the dynamical point of view.

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Comparative studies of electroless and electrochemically deposited ceria layers on Aluminum

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The wide application of protective coatings on aluminum and its alloys, deposited from electrolytes containing hexavalent chromium, although advantageous from technological and economical point of view, is discontinued. In this respect surface treatments (in hexavalent chromium free electrolytes) with lanthanide salts, are considered to be a good alternative.

The effect of ceria layers, deposited by immersion treatment or electrochemically on Aluminium 1050, non-aqueous electrolytes (absolute from aqueous and ethanol saturated and dimethylformamide) has been studied in regard to the corrosion protective ability of these systems in 0.1 M NaCl medium before and after 120 h of exposure. The "as deposited" layers were characterized by Grazing incidence X-ray diffraction (GIXRD). The morphology, structure and bulk chemical composition of the layers were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The changes of the elemental composition and chemical state of the surface layer(s) were studied by X-ray photoelectron spectroscopy (XPS). Potentiodynamic and chronoamperometric studies have been carried out aiming at comparative estimation of the corrosion-protective ability of cerium oxide films depending on the conditions of their deposition. The inclination of the system "cerium oxide layer/aluminum" to pitting corrosion has been investigated under the conditions of self-dissolution - after exposure of the samples to the corrosion medium for 120 hours time interval at a value of the anodic potential, characteristic for the process of pitting formation.

The comparison of the basic electrochemical (corrosion) parameter "corrosion current" (i_{corr}) of the studied systems followed the next order: Al > "electrodeposited ceria/Al_{substr.}" > "electroless ceria/Al_{substr.}" for the as deposited systems. The obtained results showed that the modifying of the aluminium surface by deposition (electrochemically or by electroless deposition) of protective layers leads to specific influence of the so formed effective corrosion barriers versus corrosion of the system "ceria layer/Al_{substr.}" in Cl-ions containing media after long time of exposure to the corrosive media.

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Electrocatalytic activity of ternary Ni-Co-Cu and Ni-Mo-Cu alloys for hydrogen evolution reaction in alkaline area

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Ni-Co-Cu and Ni-Mo-Cu alloys at different current densities and temperatures were electrodeposited and their influence on the alloy elemental composition was studied. The alloys ware characterized by SEM, EDS, XRF and XRD methods. The electrocatalytic activity of Ni-Co-Cu and Ni-Mo-Cu alloys for hydrogen evolution reaction (HER) in 6M KOH was estimated by Tafels plots and Electrochemical Impedance Spectroscopy. It was found a relation between the copper content in the coatings and the overpotential in Ni-Co-Cu system. The increase of the copper content in the alloys leads to drop of the overpotential. The data shows decreasing of Tafel slope in all regions with copper rising, which correspond to improving of the catalytic activity. As explanation reaction mechanism is changing, i.e. the transition from Heyrovsky to Volmer mechanism as rate determination step. Tafel plot of Ni-Mo-Cu system shows that electrocatalytic activity of this system strongly depends on the components ratio in the alloy. It was found that the Ni-Mo-Cu alloys with copper content between 15-20 wt.% possess the best catalytic properties for HER. The data of Tafel slope confirmed that Ni52Mo34Cu14 alloy shows the best catalytic activity for HER due to the lowest slope and overpotential value of -0.148V (measured at 100 mA cm-2). The value of Tafel slopes $(b_1 \text{ and } b_h)$ indicates that Tafel step of first region proceeds to Heyrovsky step for second region during HER.

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Obtaining of protective composite zinc coatings with environmentally friendly conversion films

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Zinc and zinc alloys find wide practical application for galvanizing of steel products in order to protect them from corrosion. In aggressive environments zinc coating is exhausted after a definite period of time from the steel surface and then the latter remains unprotected. Therefore, it is necessary to increase the level of protection of the sacrificial Zn layers corresponding to the current industrial standards.

The electrochemical obtaining of composite coatings with embedded different nanoparticles types gets wider development in the recent decades. According to some authors these coatings types demonstrate improved protective ability toward the substrate. Another way for increased protective ability of the zinc and its alloys is their additional treatment in special solutions for obtaining of conversion films. Similar treatment gives rise to newly appeared surface film that slows down the penetration of the corrosion processes deeply inside.

Object of the present investigation is the electrochemical obtaining of zinc and composite zinc coatings with incorporated carbon nanotubes (CNT) which have been additionally treated in environmentally compliant conversion solution the latter based on trivalent chromium compound.

The chemical composition and surface morphology of the obtained coatings were determined by using EDS and SEM analysis.

The systems zinc coating (composite) / conversion (chromite) film were characterized by means of potentiodynamic polarization curves in a model medium containing chloride ions (5% NaCl). The results obtained demonstrate the positive influence of both CNT and conversion film on the corrosion characteristics.

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Anticorrosion zinc coating containing "smart" core-shell nanocontainers with benzotriazole

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The controlled release of anticorrosion inhibitor from "smart" nanocontainers (NCs) incorporated into a zinc coating matrix can prolong the corrosion protection of steel structures [1]. Core-shell nanocontainers impregnated with corrosion inhibitor for steel benzotriazole are formed using layerby-layer deposition [2] of poly(diallyldimethyl ammonium chloride) and poly(acrylic acid) onto kaolinite particles at close to neutral pHs. Electric light scattering method and electrophoresis are employed to control the size and electrical characteristics of NCs, as well as the stability of their suspensions. The release properties of the nanocontainers are investigated using UV-spectroscopy. The inhibitor loaded core-shell NCs are incorporated into the volume of a zinc coating during electrodeposition on the surface of low carbon steel substrate to ensure additional self-healing effect in the case of corrosion attack. The surface morphology of thus obtained hybrid coating as well as the lack of aggregation of the nanocontainers during the process of electrodeposition is demonstrated by scanning electron microscopy. The influence of NCs present in the zinc electrolyte on the cathodic and anodic processes is investigated by cyclic voltammetry. The corrosion behavior of the hybrid coating at conditions of external cathodic and anodic polarization is tested with potentiodynamic measurements and the results are compared to pure zinc coating. The coating with embedded NCs revealed enhanced corrosion protection of low carbon steel in comparison with the pure zinc coating in neutral corrosion medium (5% solution of NaCl).

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Electroless deposition of copper thin layers on ABS structures

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In recent years, the specific demand for development of selective, adaptable and low cost methods has been one of the key factors for further progress in electroless deposition research. By itself, the electroless deposition is rather complex process and involves several steps of pre-treatment. The electroless deposition solutions are potentially unstable due to the spontaneous nucleation, which is a consequence of local changes in the pH or of reactions between the products and the metal ions. As a result, insoluble salts are formed into the volume of the solutions.

The aim of the results reported is to evaluate the opportunities for obtaining of thin copper layers from electroless solution that does not contain toxic reducers. A comparison is made between copper layers prepared by two different schemes of deposition: in the first scheme, a trilonic copper electrolyte with formaldehyde as reducing agent is used [1-3]. In the second scheme, the copper electrolyte does not contain formaldehyde; however the solution for activation of the substrate contains a lower quantity of Pd and a higher quantity of Sn as compared with the first scheme. In both schemes, the copper layers were deposited onto the acrylonitrile-butadiene-styrene (ABS) polymer as a substrate.

The morphology and the structure of the copper layers were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was found, that the thin gray-black colored copper layers obtained by the second scheme contain Cu_2O . These copper layers play the role of electrically conductive layers on the polymer substrate, because they allow a subsequent deposition of thick coatings by the electrochemical method [4].

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Electroless deposition of palladium nanoparticles on polysterensulfonate-doped poly(3,4-ethyelenedioxythiophene) – role of the electrode substrate

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Metal particles deposition on conducting polymer (CP) layers is intensively studied in view of their possible involvement in various applications including electrocatalysis and electroanalysis. The approach used deposit metal particles on supported CP layers main to consist in electrocrystallisation carried out under potentiostatic, pulse-potentiostatic or galvanostatic conditions. There is also another most specific opportunity to deposit metal particles on CPs by using the intrinsic redox properties of the polymer material. In this approach pre-reduced CP layers are put in contact with solutions of metal ions and a spontaneous process based on the coupling of metal ions reduction and CP oxidation takes place. This process is self-confined and depends markedly on a number of factors such as thickness and doping ions of the CP layers, concentration and ionic state (cations or anion complexes) of the source for metal reduction ([1,2] and literature cited therein).

In the present study electroless deposition of Pd is investigated by using polysterensulfonate (PSS)doped poly(3,4-ethyelenedioxythiophene) (PEDOT) layers electrodeposited on glassy carbon (GCE) or spectral graphite (SGE) electrodes. Electroless metal deposition is monitored by registering the change of the open circuit potential (OCP) of the working electrodes in the course of the coupled oxidative/reductive process. The amount of deposited palladium is determibed by anodic voltammetric stripping and the type of metal deposit is imaged by SEM.

It is established that the electrode substrate plays a significant role for the polymerisation of PEDOT-PSS with delayed formation of the PEDOT layers observed on GCE in comparison to SGE. Although the ratio of intrinsic redox charge to polymerisation charge and thus the doping level of PEDOT remains for both types of electrodes one and the same the electroless palladium deposition proceeds in completely different way. A steep OCP increase for GCE in contrast to much slower and gradual OCP change for SGE is observed and results in a ten times larger amount of metal on PEDOT-PSS/SGE. In the latter case Pd nanoparticles with mean size of about 5 nm are evenly and densly distributed on the PEDOT-PSS surface.

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Preparation and characterization of B and N co-doped TiO₂ nanotube arrays with enhanced photoelectrochemical performance

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Ordered titania dioxide nano-tube arrays (TNTA) are promising material for applications in photoand photoelectro-catalysis. Their high surface-to-volume ratio, adsorptive capacity and high photoelectrical conversion efficiency are fundamentally important for good photocatalytic properties. However the large energy band gap of TiO_2 confines its photon conversion ability to the UV spectum. Also, the relatively fast recombination of the excited electron-hole pairs lowers the

photocurrent. To surmount these drawbacks inorganic dopants are introduced in TiO_2 [1]. The aim is to extend the absorption range towards visible (Vis) light, to reduce carriers recombination and increase the rate of reduction and oxidation reactions on the semiconductor surface.

In this study a handy and unpretentious method is proposed for obtaining TNTA by anodizing a Ti Then boron introduced sheet. is via electrochemical anodic process. Consequently, annealing is conducted in nitrogen atmosphere at 500°C TiO_2 crystallization and for nitrogen imbedding. In this way well arranged nano-tubular arrays (inner diameter of 80-100 nm and length about 1 µm) are grown (Fig.1a).



TNTA(a) and photocurrent (b) on undoped, and doped anodes.

The boron and nitrogen co-doping (B,N co-doping) may exert synergistic effect due to inter-band

states formation [1], resulting in enhanced photo-excitation and extended photoactivity in the Vis light region. The photoelectrochemical behaviour of plain TNTA, N-doped and B,N co-doped anodes under Vis illumination is also demonstrated in Fig. 1b. It is clearly seen that the B,N-TNTA exhibit a better response under visible light and suggests the beneficial action of co-doping on the effective narrowing of TiO_2 band gap resulting in photogeneration of charge carriers by visible light absorption.

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Fabrication of 1D, 2D, and 3D periodic magnetic nanostructures using (electro)chemical approaches

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Periodically structured nanodimensioned materials are of fundamental interest in modern physics and technology. Artificial materials with periodic modulation of their properties allow for controlling propagation and scattering of waves such as light, phonons, electrons, or magnons.

A wide variety of 1D, 2D, and 3D magnetic nanostructured materials is accessible by advanced (electro)chemical approaches. Using self-assembled highly ordered nanoporous templates in combination with electrodeposition allows for tailoring the periodicity in all three dimensions over a wide range.

Here we present particular fabrication routes for multisegmented and multilayered magnetic nanowires, and nanomembranes with 2D and 3D periodicity as a starting point for investigating the impact of magnons on their transport properties.

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Lithographically guided electrodeposition of BiTe-based microthermoelectric coolers

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Local thermal management on optoelectronic circuits, via direct integration of micro-thermoelectric coolers (μ -TEC's) devices, can improve the performance of the device stabilizing their emitting wavelength. Furthermore, electrochemical deposition routes are well known to be fully compatible with existing integrated circuits technologies. Within this context, BiTe-based materials are one of

the most promising materials since they show high thermoelectric performance are room temperature as well as those properties can be tuned accurate control by of the electrochemical deposition conditions [2]. In addition, photolithographic techniques offers possibility to create patterns the which cavities can be used as templates for the electrodeposition process. The high lateral resolution provided by this methods allows to create µ-TEC's with high compactness of the thermoelectric active elements [3].

In this work we report on the pulsed electrodeposition of ternary $Bi_2(Te_xSe_{1-x})_3$ and $(Bi_xSb_{1-x})_2Te_3$ as n-type and p-type semiconductors, respectively. The impact of the electrochemical conditions on the morphology as well as the thermoelectric



Figure 1. Structured electrodeposition of $Bi_2(Te_xSe_{1-x})_3$ and $(Bi_xSb_{1-x})_2Te_3$ thermoelectric materials

properties of continuous films are investigated. The experimental conditions that optimized above mentioned properties on continuous films, were used for the electrodeposition on photolithographically structured substrates. However, a faster and not homogeneous growth at the edges of the structures has been observed and it can be attributed to the distortion of the electric field distribution due to the non-conductive photoresist structures. In order to overcome this issue, direct ultrasonication of the electrolyte has been carried out during deposition, homogenizing the ions inside the photoresist cavities. Finally, in this study a II-shape thermoelectric cooler has been fabricated whith electrodeposited Ni top contact between n-type and p-type legs.

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Electrodeposited micromagnets for microfluidic applications

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Microfluidic systems are of immense scientific and technological interest because of their lab-onchip a pplication potential. Biomedical or environmental analytical approaches as well as mixing, separating or pumping functions are conceivable. Focusing on fluid or particle manipulation in



Figure 1. Micromagnets designed as thin stripes in varying sizes between 10 and 100 µm (SEM cross-sectional view in a, top view in b) or as c) single bars; d,e) microfluidic (PDMS-)channel with permanent magnet on top, f) CoFe striped gradB template used for g) fluorescence measuremnet and h) PIV.

micro- or nanochannels without external mechanical forces, electric, microacoustic and magnetic fields have been proven to significantly influence the flow and particle behavior. 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. CoFe or FePt, respectively, are electrochemically deposited in micro-/nanostructured templates (Figure 1a-c). They are utilized to manipulate paramagnetic ions Mn²⁺) or superparamagnetic particles in (e.g. microfluidic devices (Figure 1d, e, h). For this purpose deposition parameters are adjusted to

achieve optimized composition, morphology and magnetic properties, such as high remanent and/or saturation polarization. Furthermore, to clarify the motion and flow behavior in microchannels in presence of a magnetic gradient field, first results of fluoresence measurements indicating the spatial distribution of paramagnetic ions inside the fluid (Figure 1f, g), potential time transients as a measure for concentration change as well as particle image velocimetry investigations (PIV, Figure 1h) supported by magnetic field gradient simulation are exhibited.

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Morphologic and Crystalline structure of Bi-Te based nanomaterials by electrodeposition

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Nowadays, more than 90% of thermoelectric module used Bi₂Te₃ alloy in modern generators and refrigeration. Thin films and nanowires gain special attention due the to predictions of significant improvements in their efficiency when they are in form of nanostructured materials [1]. Electrodepo-



sition appear as an excellent tool to fabricate these nanomaterials, due to their simplicity, by yields and high quality control and reprodutibility. In this work, the deposition applied potential effect on the morphology, stoichiometry and crystallinity of both thin films and nanowires has been conducted Bi_2Te_3 based materials. The morphology and stoichiometry was found to highly depend on the deposition potential, where by increasing it one was able to accurately control the Te% content of the deposits. X-ray diffraction measurements have shown the presence of a strong relation between the material's crystallinity and the deposition potential, where samples ranged from monocrystalline, at very low potentials, to almost completely amorphous, at high potentials. Finally, nanowire diameters were seen to diminish with the applied potential, in conjunction with the general array.

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H₂ Evolution on Pt Microelectrodes under the Influence of Magnetic Fields

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Hydrogen production via water electrolysis is an established method for energy storage. To increase the efficiency the blockage of the electrode surface by the gas bubbles during the process has to be limited. A promising solution for an increased bubble detachment is the application of an external magnetic field which is able to induce a convection inside the electrolyte due to the acting Lorentz force. For a detailed analysis of the underlying mechanisms single bubbles are the method of choice



Fig. 1: Current-time-graph for potentiostatic H_2 production, B orientated parallel to electrode surface

To analyze the impact of the magnetic field hydrogen bubbles were single produced potentiostatically at different potentials via of electrolysis sulfuric acid at a Pt microelectrode (Ø 100 µm) with a magnetic field superimposed in two different field configurations to the electrode surface for varying magnetic field strengths. The bubble behavior was visualized by a CCD camera and the electrolyte flow analyzed via Particle Image Velocimetry and Astigmatism Particle Tracking Velocimetry. Significant changes in the current signal were obtained (Fig. 1), depending on field orientation and strength, and are discussed

due to the impact of the Lorentz force induced flow around the bubble, which possibly also influences the mass transfer in the vicinity of the bubble surface. If the magnetic field is applied parallel (Fig. 1) a different bubble behavior is observed in comparison to a perpendicular applied magnetic field due to differences in the current field distribution and influence of the acting forces which results in a higher efficiency for the parallel case.

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Indenter tip calibration at shallow depths for mechanical characterization of thin films

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For the purposes of thin film nanoindentation performed with Agilent Technologies Nano Indenter G200 equipped with a diamond Berkovich tip a calibration on a silica reference sample was performed to estimate the blunting of the indentor tip and determine the contact area at shallow indentation depths, less than 250 nm, and smaller forces, less than 30 mN. This calibration is important for systems of thin film-substrate where the film is thinner than one micron such that the accuracy and repeatability of the measurements are guaranteed. Measured load-penetration data can be used in a procedure to compute important mechanical properties such as Young modulus, stiffness and hardness of the studied systems. One important variable in this procedure is the projected contact area of the diamond tip where both specimen and indentor are in first full contact, and it is related to all the other computed properties. Thus a calibration of the projected area is a crucial point in order that other parameters of interest that are derived from it are accurate and reliable.

A set of indentation tests on a silica reference sample was used to determine the polynomial coefficients of the contact area function, which is a quadratic polynomial fit to the experimental data. The fit function is based on decreasing powers of h_c , the penetration depth at first full contact, with polynomial fitting coefficients [1].

It was observed that in the course of five years of using the particular Berkovich diamond tip there is a noticeable blunting of the tip that gives different contact area for shallow depths. This was moreover confirmed by the fact that the more recent area function has steeper slope than the former thus indicating a larger contact area at identical h_c .

The actual area was used to correct the determined mechanical properties of Ce+Cu film on aluminium substrate.

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The influence of water on the cathodic voltammetric responses of choline chloride-urea and choline chloride-ethylene glycol deep eutectic solvents

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During the last decade, choline chloride-based deep eutectic solvents (DESs) have been successfully used for electrodeposition of different metals (Cr, Mn, Cu, Ag, Fe, Zn) and alloys (Zn-Cr, Zn-Sn, Zn-Ni, Zn-Mn, Ni-Co etc.) on different substrates, producing films with characteristics that are completely different from those obtained from aqueous electrolytes. Yet, the processes which occur in the blank electrolytes during the cathodic polarization of the DESs, are still not completely understood. Besides, the role of water molecules in these cathodic processes, has not been investigated in detail. It is almost impossible to avoid the water presence during the electrodeposition of metal coatings from DESs. The water is absorbed due to the high hygroscopicity of DESs, but is also added with hydrated metal salts.

This work aims to compare the cyclic voltammograms (CVs) of DESs of different compositions. The blank DESs were the mixtures of choline chloride with urea or with ethylene glycol. The CVs were recorded in electrolytes with various ratios of choline chloride, urea, ethylene glycol, and water. The increase in the concentration of a certain substance in DES results in the increase in the cathodic voltammetric peak or the cathodic current. So, it is possible to determine the species that are reduced preferentially from the mixture of the two or three substances.

The measurements taken until now, have led us to assume interesting conclusions. Namely, the species which originate from urea, ethylene glycol or water, are reduced at more positive potential than choline chloride. Besides, it seems that the electrode potential where the reduction starts is the same for these three substances (urea, ethylene glycol and water), in case that they are analysed separately. However, when both urea and water (or both urea and ethylene glycol) are present in DES, their reduction does not occur at the same potential. Instead, the water (or ethylene glycol) reduction occurs at more positive potential, which is seen as the cathodic peak, while the urea reduction in this case is hindered (shifted to more negative potential).

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Instabilities during electrochemical deposition of Sn-Co alloy from gluconate/sulfate electrolyte

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Electrodeposited tin-cobalt alloy coatings are of commercial interest as a possible substitute for Cr coatings[1] and material for Li-cell electrodes [2].

According to the phase diagram Sn-Co alloy may be composed of various intermetallic compounds depending on its metal persentage [3]. The preparation of heterogeneous coatings offers possibilities for investigation of self-organization phenomena resulting in ordered structures similar to other cobalt alloys -i.e. those with indium and antimony [3-4].

Electrochemical oscillations are observed during deposition of Sn [5] and Sn-Cu alloys [6-8]. For the first time instabilities and spontaneous potential oscillations during deposition of Sn-Co alloys are reported in the present study.

The influence of deposition conditions on the observed oscillations during deposition of tin and tincobalt alloy from a gluconate/sulphate electrolyte is studied by means of cyclic voltammetry.

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Poster Session P-27

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Selective Metallization of Laser Irradiated Biocompatible poly(dimethylsiloxane). Electroless Ni deposition

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Due to its biocompatibility poly(dimethylsiloxane) (PDMS) is an important material for the development of microelectromechanical systems or long-term, medical implants. Building up



electric circuits on PDMS surface is required. An appropriate route in this direction is the selective metallization of tracks designed by pulsed laser treatment. Induced morphology modifications and surface chemistry of irradiated PDMS are objects of this study. SEM, μ -Raman spectroscopy, X-ray micro-tomography and XPS analyses are applied. Different oxidation degrees of silicon are shown by XPS curve fitting of Si 2p and O 1s [1]. They arise as a function of laser energy absorption, due to PDMS decomposition. The irradiated ablated parts become hydrophilic, whereas the rest of the material remains hydrophobic. This is a prerequisite for selective metallization of the tracks.

Different operation regimes of laser irradiation are employed and their suitability for electroless deposition is assessed. Electroless deposition of Ni in baths with hydrazine as reducing agent is applied for metallization. When femtosecond (fs) pulsed laser is used for tracks design (a), Ni is forming spiky coatings (b). The latter Ni morphology is related with impedance desired in some applications. It was

demonstrated that fs pulsed laser can be tuned so as to allow successful electroless metallization without preliminary sensitization and activation [2]. It was found the lapse between the laser treatment and electroless deposition is not a critical process parameter.

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Effect of anodic aluminium oxide structure on the electroless nickel deposition into nanopores

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The electrochemistry proposes an exceptional capacity for formation of different nanostructures as for example the self-ordered nanoporous layers and the electroless or electrodeposition of 1D nanowires in this template. One similar object is the anodic aluminum oxide which is a self-organized material with uniform and parallel nanopores. The diameter of the pores can be very precisely controlled by experimental conditions of electrochemical oxidation such as a nature and concentration of acid, tension, temperature, etc. The deposition of metals into the pores or on films in 3D substrates like porous anodic alumina is of great interest from fundamental point of view as well as for its practical applications.

In the present work, three different nanoporous layers (10 µm thick) have been obtained by anodizing of aluminium in sulfuric, oxalic, and phosphoric acids at tensions as follows 20, 40 and 120 V. The average pore diameter of produced anodic aluminium oxide (AAO) within these tensions are respectively 20, 40 and 100 nm. The nanoporous templates were catalyzed with palladium and then nickel was electroless deposited into/on the oxide layer. The elemental composition along the cross-section of the samples was identified by EDX spectroscopy in modes of line scanning and in point.

Within the smallest pore diameter of 20 nm, nickel has been registered only on the surface. As an example, at 1.5 μ m in depth from the surface, the nickel is about 0.5 at.%, and above 2 μ m of depth, no nickel has been registered at all. Within pore diameters of about 40 nm, traces of nickel were found at 7 μ m depth, and within an average diameter of the pores of about 100 nm, the nickel content is high (above 5.7 at.%) up to the Al/Al₂O₃ interface.

The SEM observations of layer structures $Al/Al_2O_3+Ni/Ni$ with pore diameters 40 and 100 nm clearly show that the nanoporous structure remains the same. This indicates that nickel is being deposited comparatively uniform on the walls of the pores. Filling of the pores with metal is observed only at the mouths of the pores (up to 0,5 μ m in depth) even in case of the template with the widest pores. Therefore, the developed technology for electroless nickel deposition with preliminary palladium activation of the AAO template, seems appropriate for obtaining of nanotubes.

In conclusion, the experimental results show that the nickel content gradually decreases along the pores and the nickel penetration depth depends on pores diameters.

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All-electrochemical approach towards ON/OFF switching of magnetism in FeO_X/Fe nanostructures at room temperature

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Electric field control of magnetism promises new and energy saving possibilities for the development of nanoelectromechanical systems and spintronic devices. Recently, a novel approach based on voltage-induced ion migration and electrochemical oxidation and reduction has emerged to control the magnetism in oxide/metal heterostructures [1,2]. In our preceding works we could show that in the system FeOx/Fe in a aqueous KOH-based electrolyte, oxidation and reduction reactions readily occur at the solid/liquid interface and can give rise to enormous and reversible magnetic property changes [3,4].

The present study demonstrates that nearly complete and reversible voltage-induced ON/OFF switching of magnetism can be obtained in granular FeO_x/Fe thin films polarized by few volts in 1 M KOH solution. FeO_x/Fe films of a nominal thickness of 2 nm were prepared by electrodeposition on a Si/Cr/Au substrate. The cross-sectional HRSEM image of an as deposited Fe film reveals nanogranular morphology. The magnetic property changes during polarization were resolved by in-situ measurements of the anomalous Hall effect at room temperature. The application of a reduction potential of -1.26 V results in a strong increase in J_S, which is related to



the reduction of the native surface iron oxide. At the subsequent oxidation step at -0.20 V, J_S is decreased again. The observed maximum voltage-induced change of J_S 90 % is much higher than in sputter deposited films with comparable nominal thickness [3]. In summary, the use of electrodeposited films presents an all-electrochemical approach for magneto-ionic effects without requiring vacuum technology.

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ZnO/TiO₂ Core/shell Nanowire Networks Fabricated by Ion-track Technology and Atomic Layer Deposition

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The compact design, mechanical stability and high surface area of 3D nanowire-based hierarchical systems can be advantageous for example to facilitate efficient light absorption and charge carrier transport in photoelectrodes [1-5] and optical elements, to enhance the performance of gas sensors [6,7] batteries [8,9] and supercapacitors [10] or to achieve high electric field confinement and enhancement in 3D plasmonic hollow nanocavities [11], as well as for computer and chip technologies [12].

The aim of this work is the synthesis and characterization of ZnO nanowire-based structures applying ion-track technology in combination with electrochemical deposition. Additionally, atomic layer deposition of TiO₂ is used to produce core/shell structures as protection layers from corrosion during electrochemical measurements. The number density and diameter of the nanowires in the network were optimized in order to obtain mechanically stable 3D building blocks exhibiting a high surface area. The crystallographic properties were studied by XRD, high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and high-angle annular dark-field (HAADF) imaging. Knowledge drawn from these investigations is crucial for the implementation of these 3D nanoarchitectures into devices, including photodiodes and -electrodes.

Core/shell ZnO/TiO₂ nanowires arrays and nanowire networks were prepared by coating the samples with thin TiO₂ layers by atomic layer deposition (ALD) at 110 and 250°C, respectively. Electron energy loss spectroscopy (EELS), HRTEM and HAADF studies confirm the conformal and homogeneous coating of the wires. The coating at 110°C results in amorphous TiO₂ shells, while the ALD process at 250°C leads to a crystalline TiO₂ layer with anatase phase consisting of mainly (101) planes.

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EDNANO12

12th INTERNATIONAL WORKSHOP ON ELECTRODEPOSITED NANOSTRUCTURES

March 16-18, 2017 – Sofia, Bulgaria

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