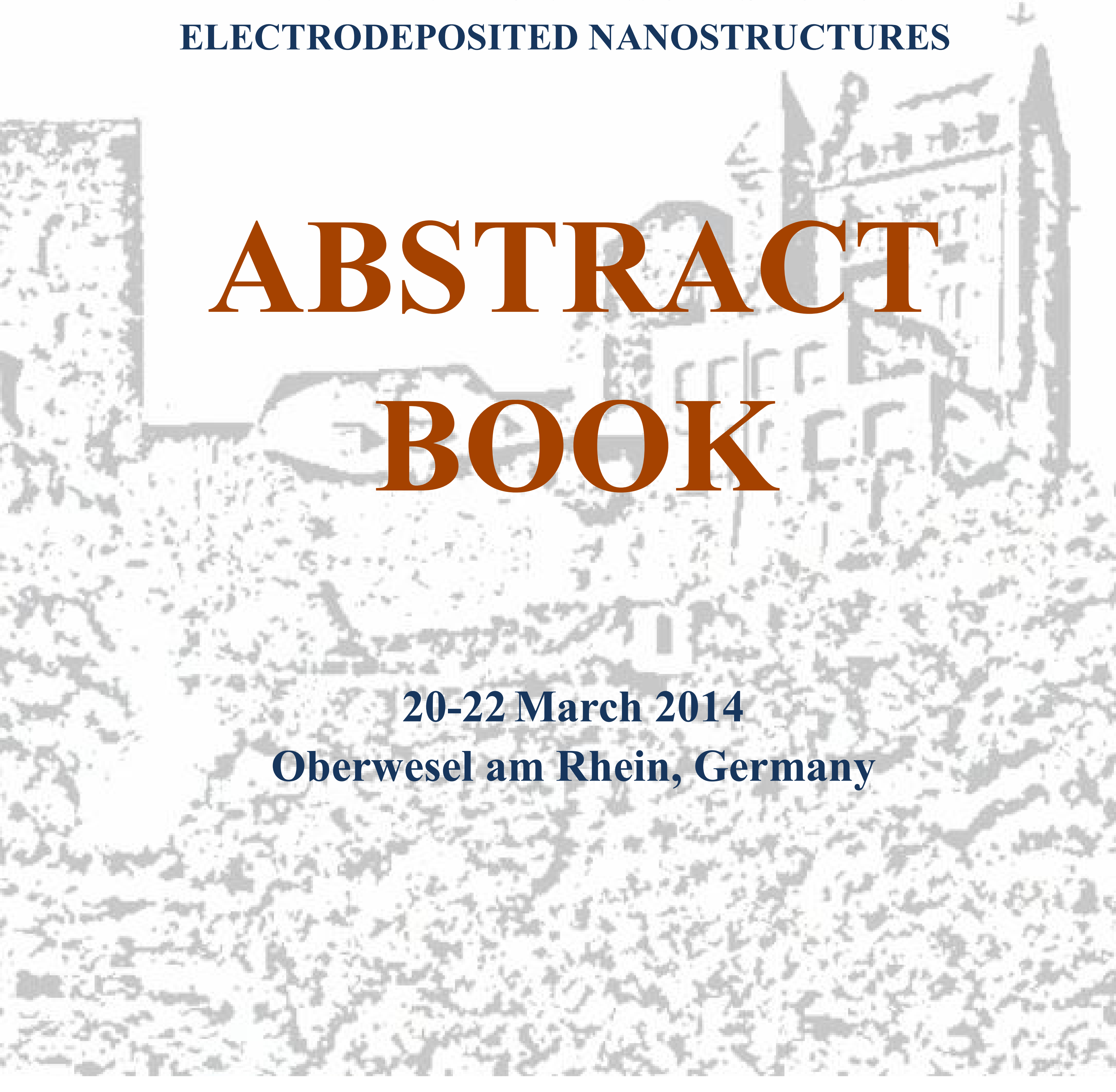
10th INTERNATIONAL WORKSHOP ON ELECTRODEPOSITED NANOSTRUCTURES

ABSTRACT BOOK

20-22 March 2014
Oberwesel am Rhein, Germany



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ABSTRACT BOOK

Organizers: Dr. Maria Eugenia Toimil-Molares, Dr. Ina Alber, Janina Krieg, Liana Movsesyan, and the Nanowire Group at GSI Helmholtz Centre, Materials Research Department

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Electrodeposition in non-aqueous media

Preparation, structure and giant magnetoresistance of electrodeposited Fe-Co/Cu multilayers

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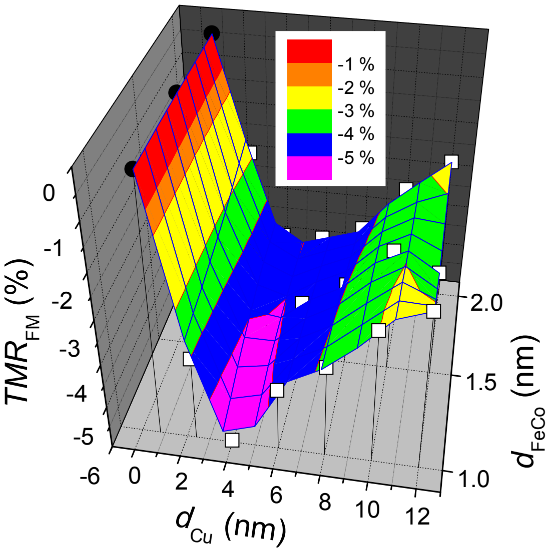
Among multilayers prepared with physical methods, Fe-Co/Cu multilayers have simultaneously large giant magnetoresistance (GMR) and low GMR saturation fields. No systematic studies have been carried out on the GMR of electrodeposited (ED) multilayers in this system since the elaboration of a method for the optimization of the Cu layer deposition potential, which is a prerequisite for a quantitative control of the individual layer thicknesses in ED multilayers [1]. The Cu layer deposition potential was found to depend on the relative iron concentration in the bath. The dependence of the magnetic layer composition on the ionic ratio $Fe^{2+}/[Fe^{2+} + Co^{2+}]$ was also mapped out. An X-ray diffraction study of ED Fe_5Co_{95}(1.5nm)/Cu(d_{Cu}) multilayers with d_{Cu} ranging from 0.8 nm to 10.0 nm revealed an fcc structure. For most of the multilayers, a weak superlattice satellite reflection on the low-angle side of the main peak could be identified from which bilayer lengths about 10 to 20 % larger than the nominal values could be deduced. The room-temperature magnetoresistance was studied in detail as a function of the individual layer thicknesses. Multilayers with Cu layer thicknesses above about 1.5 nm were found to exhibit a GMR behavior with a maximum GMR of about 5 % and a typical saturation field of 1 kOe. The GMR magnitude decreased with increasing Fe-content (z_{Fe}) in the magnetic layer. The spacer layer thickness evolution of the MR data was established in detail after separating the ferromagnetic and superparamagnetic GMR contributions and a comparison with literature data on both physically deposited and ED [2] Fe-Co/Cu multilayers will also be made. As a general conclusion, it could be established that ED Fe-Co/Cu multilayers do not exhibit an oscillatory GMR behavior with spacer thickness, similarly to other ED multilayer systems (see figure, $z_{Fe} = 5$ %).



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Magneto-thermopower and giant magnetoresistance measurements on single multilayered Co-Ni/Cu nanowires

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The magneto-thermopower (MTP) is linked to the giant magnetoresistance (GMR) of individual multilayered Co-Ni/Cu nanowires with varying Cu thickness. Both magneto effects are studied temperature dependent in perpendicular magnetic fields leading to cross plane GMR effects of up to 15 % at RT. This is a typical effect size for electrodeposited nanowires - recipe published by Tóth *et al.*[2] A linear dependence between thermopower S and conductivity σ of the nanowires – with the magnetic field as an implicit variable - is found at a wide temperature range (50 K to 325 K). This observation is in agreement with the Mott formula with an additional thermopower offset, which allows the estimation of the absolute Seebeck coefficient of the contact material. By drawing this conclusion equal GMR and MTP values have to follow, as already described by Conover *et al.*[1]

The linear behavior – S vs. σ – and the Mott formula are used to calculate the energy derivative of the resistivity, which can be further correlated to the transmission function serving as a starting point in theoretical models. Magneto-thermal conductance measurements are planned to complete the characterization of the spin caloritronic properties, in particular to validate the Wiedemann-Franz law in cross plane GMR structures.

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Electrochemical deposition of CoNi Alloy nanowires and multisegmented stacks in hard-anodic alumina templates

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Co-Ni alloy nanowires can be designed with tailored magnetic properties by the proper combination of low and high magnetocrystalline anisotropies corresponding to the *fcc* Ni and *hcp* Co phases, respectively [1]. Additionally, the anomalous electroplating behaviour of the Co-Ni alloys results in a preferential deposition of Co atoms with respect to the Ni ones at low deposition potentials [2], which allows for tuning the composition of the alloys either by varying the electroplating potential or the electrolyte composition. In this work we have electroplated $Co_{(100-x)}Ni_x$ ($5 \leq x \leq 100$) nanowires of about 150 nm in diameter into the pores of hard-anodic nanoporous alumina membranes, as well as multisegmented nanowires made of $Co_{54}Ni_{46}/Co_{85}Ni_{15}$ stacks, with an approximate length of 300 nm per segment. The nanowires morphology, crystalline structure and chemical composition were characterized by means of SEM, TEM, EDS and XRD techniques. VSM magnetic hysteresis loops were measured along both the parallel and perpendicular directions with respect to the nanowires axis and they were correlated with the microstructural features of each alloyed/multisegmented system. Our results point out that tuning the composition of the alloy enables adjusting the magnetic anisotropy of the nanowires. Furthermore, the array of multisegmented stack nanowires does not clearly show an easy magnetization axis due to the strong competition between shape and magnetocrystalline anisotropies, together with the effect of the magnetostatic dipolar interactions among adjacent barcode nanowires.

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Electrodeposition of $Fe_{50}Pd_{50}$ nanowires and their characterization

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$Fe_{50}Pd_{50}$ nanostructures with an ordered $L1_0$ crystal structure attract lots of attention due to their high magnetocrystalline anisotropy (280 kA/m), which makes these materials interesting for high density perpendicular recording media. The controlled growth of metal nanowires has been a topic of many investigations in the last few years, because of their potential application as high density magneto recording media or in nanoelectronic devices.

In this study densely packed near equiatomic 3.5 μm long Fe-Pd nanowires were synthesised via template assisted electrodeposition method. The Fe-Pd nanowires were deposited from single electrolyte based on $FeCl_3$, $PdCl_2$, $(NH_4)_2C_6H_6O_7$ and $NH_{3(aq)}$ with pH 9 into Al_2O_3 membranes with the pore diameter 200 nm (AAO) sputtered with 600 nm of Au and electrochemically deposited Au. Prior to electrodeposition of nanowires, cyclic voltammetry was performed in order to investigate the deposition process. Multiple cycling reveals the real behaviour during the deposition process. As soon as the first monolayers are deposited, deposition proceeds at more positive potentials (150 mV overvoltage). In order to deposit homogenous nanowires with consistent composition along the length of the wires, several parameters, such as wetting of the AAO template, gold sputtering, electrolyte concentration and pulse plating were investigated. In addition homogenous nanowires were deposited with potentiostatic and pulse plating method. The as-deposited nanowires and annealed nanowires were characterized with the FEG-SEM/EDS, MFM, XRD and VSM methods respectively. The as-deposited nanowires had an *fcc* crystal structure and were magnetically soft ($H_C \approx 5$ kA/m) with an easy axis aligned perpendicular to the nanowire axis, due the high porosity of the AAO template leading to a large contribution of the dipolar interactions, that cancelled out the contribution of the shape anisotropy [1]. Furthermore, MFM study of a single nanowire shows an opposite behaviour, where the easy axis of magnetisation is aligned along the long nanowire axis and $H_C \approx 50$ kA/m, due to the contribution of the shape anisotropy. In addition, to promote the ordering into the $L1_0$ phase, annealing in the temperature range of 400–700 °C for 1–9 h in Ar + 7 % H_2 was performed. The highest coercivity of 130 kA/m was achieved by annealing at 600 °C for 4 h, which makes the Fe-Pd nanowires appropriate for nanostructured magnetic recording media.

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Influence of electrodeposition conditions on the composition and surface magnetization processes of Fe-Ga magnetostrictive nanowires

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The magnetoelastic properties of Fe-Ga alloys are very sensitive to the microstructure, the solubility of Ga in bcc α-Fe and the fabrication process [1], these effects being more prominent for Fe-Ga electrodeposited alloys [2].

In this paper, we are presenting our latest results on the influence of Ga content on surface magnetization processes in Fe-Ga magnetostrictive nanowires prepared by pulse electrodeposition into alumina templates with nanopores of 300 nm in diameter and 55 μm in length. The deposition potential, concentration of the surfactants and pH of the electrodeposition bath all concur in the composition of the nanowires. The EDX analysis is showing a variation in the composition along the nanowires length, from $Fe_{55}Ga_{45}$ at the bottom of the template (where the electrodeposition process starts) to $Fe_{80}Ga_{20}$ at the top (where the concentration of Ga^{3+} ions is reduced). The MFM images taken along the nanowires length are showing magnetic inhomogeneities in the top part of the nanowires (10-15% from the total nanowires length of 50 μm), and more homogeneous magnetic structures at the bottom part. The different magnetic behavior along the nanowires is also proved by the local magnetic loops measured by longitudinal magneto-optical Kerr (MOKE) effect (the rotation of the plane of polarization is proportional with the magnetization component parallel with the plane of incidence), using a polarized light generated by a He-Ne laser with a diameter of 10 μm. An applied field of maximum 3 kOe was applied along the nanowires length using an electromagnet. The hysteresis loops taken at each 10 μm along the nanowires length, indicated a progressive decrease of the coercive field from 400 to 250 Oe with the Ga content decrease from 45 to 20 at.% (the last one is the eutectic composition).

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Tuning the nanostructures architecture and composition using template assisted electrodeposition

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Unique and interesting phenomena are expected both from fundamental and technological points of view as the geometrical dimensions of the devices become comparable to the electron mean free path or the domain-wall width. In particular, 1D systems composed of nanowires (NWs) and nanotubes (NTs) with reduced dimensions (few nanometers) can exhibit considerable changes in their physical properties, including quasi-ideal magnetization reversal, quantized spin transport, or electron localization effects which make them potential candidates for technological applications (electronics, energy harvesting and biomedicine).

In this work we will report the groundwork performed in the growth of metallic and magnetic nanotubes, nanowires, segmented nanowires, and modulated nanowires by DC electrodeposition inside porous anodic alumina (PAA) templates. We will show that performing DC electrodeposition, several materials can be deposited in free-standing PAA membranes, such as NWs and NTs of single elements (Ni, Co, Fe), NWs of alloys (CoNi), multilayered NWs (Ni/Cu, Ni/Au), and modulated nanostructures. DC electrodeposition has thus proven to be a powerful technique, enabling substantial control of the nanostructures composition and crystallinity, even allowing compositional modulation along the wires. However, PAA filling using a DC electrodeposition technique is not a very suitable method for industrial applications due to the required laborious template processing and its applicability is limited to free-standing thick membranes (> 20 μm). In this way, we will also present results on the pulsed electrodeposition method as an alternative technique to grow NWs of single elements and will conclude by presenting the perspectives and limitations of the pulsed method in the fabrication of more complexes architectures like multilayered NWs, alloys and modulated nanostructures.

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Nanocrystalline nickel micro-structures for thermal micro-actuators

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Micro galvanic processes are the basis of the electro deposition of thermal actuators, and require knowledge of the electrochemical fundamentals as well as numerical electrochemical process simulation for adjustment since the defined electro deposition of the nickel matrix is crucial for the properties and functionality. Especially, realization of high aspect ratios requires the application of sophisticated plating techniques such as pulse reverse deposition. The pulse plating process is adjusted using the results of electrochemical numerical simulation routines, visualizing the (local) potential field and the current field line distribution as a function of the applied electrochemical parameters. Compact, completely void free structures can be obtained by realizing nano-crystalline nickel deposits via the pulse plating process. MEMS structures were designed to convert the thermal expansion of the material into an in-plane deflection.

A custom made measurement setup, consisting of a sealable chamber, a Peltier element with a temperature control unit, and an optical microscope was used for measuring these deflections at different temperatures. A set of cantilever structures with different lengths was used to evaluate the Young’s modulus and the vertical stress gradient of the plated materials. Additional, finite element simulations were carried out to determine the thermal expansion coefficient of the plated Nickel, by fitting the simulation and the measurement results.

A microgalvanic pulse plating process for plating Ni was developed for this purpose. The plated material itself has closed surface and side walls. To evaluate the aspect ratio of the process, a set of beams with decreasing width was used. It has been shown that the lithography of the resist, defining the structures, was the limiting process for the aspect ratio. A ratio of 1:6.4 was achieved and Ni was successfully deposited also into the small features. It can be assumed that the galvanic process can achieve even higher aspect ratios.

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Relationships between microstructure and contamination in nanocrystalline Ni-based coatings

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Nanocrystalline electrodeposited coatings have been the subject of numerous studies due to their resistance against corrosion and their particular mechanical properties. However, the superior corrosion resistance of lower grain size metals, particularly at the nanometer scale, has not been yet clearly established [1]. Actually, as grain size decreases, other parameters like crystallographic orientation, chemical contamination, internal stresses…, which can affect the corrosion resistance, are also modified. The aim of our approach is to better understand the influence of the microstructural parameters, mainly grain size, on the corrosion resistance. In order to achieve this objective, a careful characterization of the metallurgical states of electrodeposited nanocrystalline coatings is needed. Additive free nickel sulphamate and citrate-ammonium baths are used to obtain pure Ni and Ni-W alloys, by applying direct and pulse currents. A combination of several microstructural techniques at different scales (SEM, XRD, EBSD, TEM) is used to characterize the morphology, the grain size, the crystallographic texture and the nature of grain boundaries. These complementary techniques permit to define transition scales that are necessary to discuss the physical meaning of the different microstructural features [2]. The chemical contamination especially by light elements is characterized by SIMS and hot extraction analysis. In additive free sulphamate bath, regardless of electrodeposition regime (direct currents or pulse plating), grain size refinement and crystallographic texture modifications are associated with higher contamination mainly by light elements (O, H, C, Cl…). In NiW alloys the link between chemical contamination and grain size is more complex, and the presence of high amounts of impurities (H, O, N) is correlated with morphological features (colonies boundaries, cracks…).

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Electrodeposition of bismuth thin films on n-GaAs

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Bismuth (Bi) is an interesting semimetal for studying Quantum Size Effects (QSE) [1-2] due to its large Fermi wavelength (λ_F = 40-70 nm at room temperature). In order to study QSE in Bi thin films, it is compulsory grow high-quality films onto semiconducting substrates, so as to avoid current leakage during transport measurements. In previous studies about Bi growth, electrodeposition has proved to be a suitable technique [3-4]. However, electrodeposition on semiconductors might be complicated due to the particular electronic properties of this kind of materials.

In this work we have studied, through the Bi^{3+}/n-GaAs(111)B system, an effect inherent to the electrodeposition of metals on n-doped semiconductors, especially when metals have a reduction potential more positive than the H^+ reduction potential. Cyclic voltammetry (CV) scans and energy band diagrams suggest the presence of a blocking layer of adsorbed hydrogen that hinders a good nucleation of Bi (figure 1a). Moreover, we have studied the effect of the substrate orientation on the films growth (figure 1b and c), since the surface composition and the surface atomic arrangement are directly related to the electrode reactivity.

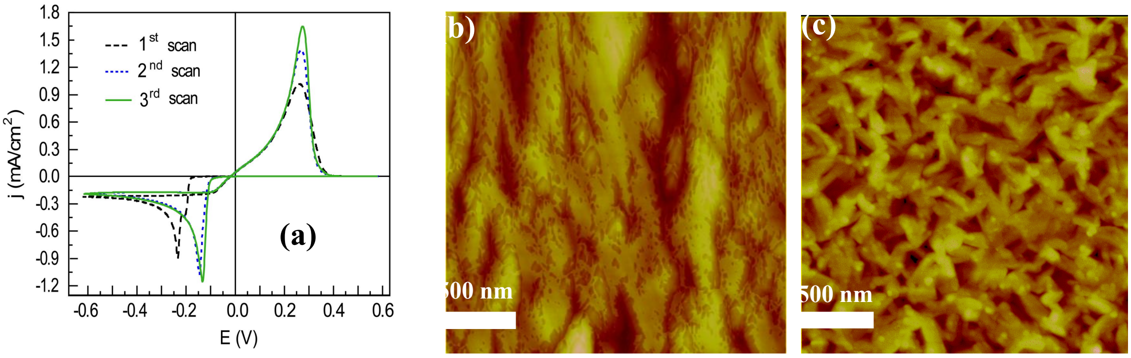

Figure 1. a) CV scans for n-GaAs(111)B in a Bi^{3+} solution under darkness conditions. AFM images of 50 nm Bi thin films electrodeposited under same conditions on n-GaAs substrates with orientation b) (110) and c) (111)B.

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Electrodeposited Cuprous Oxide as a promising Solar Water Splitting Photocathode

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The possibility of producing chemical fuels from solar energy has become increasingly attractive as sustainable, clean and efficient solution to our ever-growing energy demands. Photoelectrochemical (PEC) water splitting has been much improved since the first reports by Boddy [1] and by Fujishima and Honda [2] and nowadays researchers aim to find inexpensive, efficient and stable materials to perform PEC water splitting. [3] Cuprous oxide, Cu_2O, is very interesting since it has a 2 eV bandgap with favorable energy band positions, good conductivity and it can be processed with low-cost methods such as electrodeposition. [4] Cu_2O has been proven an efficient material with current densities up to 7.5 mA cm^{-2} under AM 1.5 illumination and biased at 0 VRHE 5 nevertheless it is not stable in contact with the electrolyte, decomposing completely after few minutes. The best-reported approaches to extend its stability refer less than one hour of photocurrent with a variation loss < 10 %. For real applications, much more than a few hours are required and new strategies are needed to overcome this limitation.

In this work, we present three different approaches to enhance the Cu_2O stability up to 60 h with only 10% loss. First we present the DC electrodeposition method to fabricated Cu_2O thin films. Then, a new catalyst was implemented that offers great Faradaic efficiency as well as extends the stability of the device up to 8 h (chopping conditions). [5] New overlayers were also tested together with heat treatments that protect the semiconductor surface from the electrolyte more efficiently. These overlayers deposited by atomic layer deposition (ALD) offer a solid and homogeneous cover to the semiconductor. These new results open a much needed window to make this semiconductor a strong competitor for solar water splitting applications.

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Journal of Visualized Experiments:
Nanowire synthesis and photocatalytic H_2 formation

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The *Journal of Visualized Experiments* (JoVE) is a relatively new journal that is devoted to publishing scientific research in a visual format to help researchers overcome two of the biggest challenges facing the scientific research community today; poor reproducibility and the time and labor intensive nature of learning new experimental techniques.

- JoVE allows authors to publish experiments in all their dimensions, overcoming the inherent limitations of traditional, static print journals, thereby adding an entirely new layer to the communication of experimental research.
- Visualization greatly facilitates the understanding and rapid reproduction of both basic and complex experimental techniques.

JoVE recently accepted our procedure explaining templated electrodeposition of axially segmented Ag|ZnO nanowires and coaxial TiO_2-Ag nanowires, and the detection of H_2 gas using a Pd-based sensor. In the video, a very simple and low-tech procedure for the synthesis of these nanowires will be explained in detail in such a way that it is very useful to any researchers new in this field. In addition, we also show how you can detect the formation of H_2 during photocatalytic water splitting experiments with the use of a Pd-based H_2 sensor, so that an expensive gas chromatograph is not needed for qualitative H_2 detection.

The procedures we explain are based on two of our previous publications [1,2].

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Electrochemical deposition of ZnO nanostructures with controlled size and geometry in etched ion-track membranes

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We present the synthesis of various ZnO micro- and nanostructures, such as parallel arrays of cylindrical and conical nanowires (NWs) and 3D nanowire networks (NWNWs) consisting of interconnected wires. These structures are potentiostatically electrodeposited in polycarbonate etched ion-track membranes, which is a very suitable technique for fabrication of nanostructures with small size and high surface-to-volume ratio [1,2]. ZnO nanostructures with different lengths (up to 30 µm) and diameters (between 80 - 300 nm) are grown from an aqueous solution containing a zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) with concentrations of 0.01 M, 0.1 M [3] and 3 M. Different potentials ranging between U = -0.5 V vs. Ag/AgCl and U = -1.4 V vs. Ag/AgCl and temperatures varying between T = 60˚C and T = 80˚C are applied and adjusted for each type of ZnO structure. Size and geometry of these micro- and nanostructures are determined by scanning electron microscopy (SEM). The influence of growth parameters on the nanostructures morphology is analyzed. Further structural and compositional analysis is performed by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). First electrical measurements of contacted NW arrays demonstrate semiconducting behavior, as expected.

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Electrodeposition of Si and Ge nanowires (NWs) and Nanotubes (NTs) using room temperature ionic liquid

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Silicon and Germanium NanoWires (NWs) or NanoTubes (NTs) have numerous applications in hydrogen storage, gas sensing, field emission, Li-ion Batteries, optoelectronics and so on. However, the preparation of silicon and germanium still requires constraining deposition conditions such as high vacuum and high preparation and the control of the geometry, composition (alloying or doping for example) is time consuming as it involves the development of one growing process per materials. Thus, it is not easily transposable to a future industrial large scale synthesis. In consequence, finding an alternative method for growing such NWs or NTs of different composition at a low cost, under room-temperature conditions and with easier growing process is a real challenge in the next few years.

In 2008, our group shows the possibility of growing Si NWs through a simple, innovative, original and alternative technique[1,2]: electrodeposition in Room Temperature Ionic Liquids (RTILs) which enables to prepare silicon at room temperature and under atmospheric pressure. Thanks to this study we show an improvement of the method to grow well organized Si, Ge NWs but also NTs at a large scale and SiGe alloy NWs or even Er doped SiNWs. While it is impossible to electrodeposit silicon using aqueous solvents, the wide electrochemical window of several RTILs compared to water makes possible the electrodeposition of Si, Ge, SiGe alloys or doped-Si materials. The simultaneous use during the growth of polymer or alumina membranes with pores of controlled diameters, lengths and densities lead to the growth of NWs with diameters between 15 and 400 nm.

By using RTILs and membranes, it is possible to grow pure Si and Ge NWs but also SiGe alloy NWs with various compositions and Si:Er doped NWs only by controlling the ratio between $SiCl_4$, $GeCl_4$ or $ErCl_3$ in the solution and the deposition potential which makes this method very competitive compared to classical PVD or CVD experiments. From an electrochemical point of view, an important difference between aqueous solvent and ionic liquid is the viscosity (it can be eighty times more viscous than water), strongly correlated to the ionic conductivity and ionic diffusion. Considering this, many characteristics of the synthesized nanostructures are influenced by the ionic diffusion of ions inside the nanopores. To have an influence on the diffusion regime, nanostructures have been grown at various temperature using different deposition regime (steady state current deposition or pulse deposition) with various membrane thickness and we have shown that it is also possible to grow NTs instead of NWs by carefully choosing the growth parameters. Finally, the correlation between the structural characterizations and the promissing optical properties of the NWs will be discussed.

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Non-aqueous electrodeposition of Ni and Fe-Ni alloys

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Electrodeposition is a widely used technique to produce Fe-Ni alloys. The importance of the Fe-Ni alloys stems mainly from their magnetic properties, especially the low coercivity. The first review of this topic was published as early as in 1962. Electrodeposition in non-aqueous media is a research area with great perspective because it opens up the preparation of metallic alloys which cannot be electrodeposited from aqueous media in the stability range of water.

Our goal was the electrodeposition of Fe-Ni alloys and the study of the deposition preference by non-aqueous electrodeposition. The possibility of elemental Ni and Fe deposition was investigated in methanol and methanol/polyvalent alcohol solvent mixtures. Beside methanol, the second solvent component was ethylene glycol, 1-3-propanediol or glycerin. The dissolved anhydrous metal salts were the divalent chloride or bromide compounds of the constituent metals.

Cyclic voltammetry was used to establish the potential range for metal deposition. The deposition of both Fe and Ni started at around -900 mV vs. saturated calomel electrode. The deposition rate of the metals increased up to -1400 mV. However, at more negative potentials, the deposition rate of the metals decreased due to the decomposition of the solvent. The stripping peak of Ni was easily observed on the anodic-going scans, but neither stripping nor oxidation to Fe(III) species could be seen for Fe.

The electrodeposition from alcoholic media was compared with the electrodeposition from aqueous media from the aspect of the codeposition mode. The role of the solvent components and the anions on the codeposition mode was investigated in detail. The composition as established from EDX measurement was determined as a function of the deposition conditions. The structure of the deposit was also investigated with X-ray diffractometry.

Electrochemical Copper Deposition from an Ethaline-$CuCl_2.2H_2O$ DES

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Electrodeposition of copper is carried out using acidic or basic aqueous systems, which are coming under scrutiny for their environmental impact. In the past decade researchers have proposed ionic liquids (ILs) as alternative to such aqueous solutions. An IL can be defined as a mixture consisting solely of cations and anions with a melting point of 100°C and below. Although a variety of ionic liquids are available in the market, for practical metal plating purposes, choline chloride (ChCl) based ILs [1] is one of the cheapest and easily accessible. Choline chloride (ChCl) based ILs consist of $C_5H_{14}NOCl$ with a hydrogen bond donor (HBD) such as $C_2H_6O_2$ (ethylene glycol) to form a deep eutectic solvent (DES) or melt. Although there have been a variety of studies examining metal deposition from ChCl-based DES, there is little information on the performance of these electrolytes for long term practical metal deposition.

In this work Cu electroplating was carried out using an ethaline-200 melt, which is a 1:2 ratio of choline chloride and ethylene glycol, by potentiostatic and galvanostatic methods. Hydrated cupric chloride was added to the pure ethaline melt. Polarisation data for cupric ion reduction to copper was collected using an RDE to determine where metal deposition was feasible. For long term experiments, copper was deposited at a low carbon steel substrate up to a thickness of 15 μm. All deposits were analysed using standard materials analysis techniques. In order to detect changes in the ethaline melt, a separate experiments were carried out, where a number of plating operations from the same bath was performed. Changes in solvent coloration, precipitation and any associated changes within the deposit were monitored during this time period.

Smooth Cu deposits were obtained at 4.7×10^{-3} A/cm^2 using 0.2 M $CuCl_2.2H_2O$ at 25 °C at a current efficiency of (95±5)% at a rotation speed of 700 rpm. XRD analysis of the deposit showed a polycrystalline face centered cubic structure with (111) texture. The crystalline size was 66±10 nm with some internal strain. EDX analysis showed the presence of carbon and chlorine with copper in the deposit, which was due to the break-down of the DES. The long term deposition experiments showed that the bath was stable when a soluble anode was employed, and became unstable when an insoluble anode was used. This was due to other reactions proceeding at the cathode.

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Friday March 21st, 2014

Musiksaal

Alloys

Nanotubes and templates

Thermoelectric nanostructures

Electrochemical applications

Electrodeposition of Au, AuAgCu, and AuAgCuNi plasmonic materials from non-cyanide solutions

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New plasmonic applications create a demand for materials capable of achieving specific optical, electrical and mechanical properties. Pure gold shows excellent plasmonic optical properties at room temperatures, but is susceptible to deformation caused by high energy densities encountered in plasmonic devices [1].

For this work, gold thin films were prepared by electrodeposition from a thiosulfate-sulfite plating solution while AuAgCu and AuAgCuNi gold alloy films were prepared using a thiosulfate-ammonium sulfate solution [2,3]. Gold alloy films potentially have greater stability while maintaining gold's desired plasmonic behavior. The electrochemical behavior of Au deposition from fresh and 2 year aged plating solutions was also studied using Au and Pt electrodes and found to be quite different.

We studied the effect of deposition parameters on film properties relevant to plasmonic applications such as roughness, grain size, index of refraction and extinction coefficient which can be used to predict viability as a plasmonic material. Thin film and patterned samples were annealed at temperatures up to 400°C to replicate the temperatures encountered in applications such as Heat Assisted Magnetic Recording (HAMR). While Au films showed poor thermal stability, the addition of Ag, Cu and Ni were able to increase the stability of the material.

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Synthesis of AuAg Nanowires for Plasmonic Applications

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Au and Ag nanowires are attracting great attention due to their interesting plasmonic properties. The excitation of surface plasmons using visible or infrared light generates very high field enhancements on the wire surface, highlighting Au and Ag nanowires as very promising for sensing applications using surface enhanced Raman and infrared spectroscopy. It has been previously shown that the formation of small hotspots in the nanostructures, such as small gaps or pores, leads to even higher field enhancements. [1] The selectivity and sensitivity of plasmonic sensors can be improved if strategies to adjust precisely the surface plasmon wavelength are developed. For this, a high controllability of wire dimension, composition, and surface morphology as well as of the size of the hotspots is necessary.

We have synthesized AuAg alloy and segmented nanowires using electrodeposition from a single-bath electrolyte in ion-track etched polymer templates. [2] The role of applied voltage and electrolyte composition on the nanowire structural and compositional characteristics was investigated by various methods, such as scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction. To form hotspots for plasmonic applications, the AuAg alloy wires were treated with nitric acid resulting in rough or porous nanowires depending on the initial alloy composition. High-resolution analysis by transmission electron microscopy (TEM) was performed before and after dealloying to obtain a deeper insight into the formation process. Finally, by treating the segmented nanowires with nitric acid, nanogaps as small as 5 nm were created and their plasmonic properties were investigated using electron energy-loss spectroscopy using scanning TEM. [3,4]

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Electrodeposition of supersaturated CuAg alloys

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The application of electrodeposited copper to the manufacturing of electrical contacts in microelectronic is nowadays widespread. However, the use of this metal presents problems when high mechanical properties are required. Another problem can be found in electromigration, a phenomenon that is significant in structures of reduced section. To improve these two aspects a possibility can be the addition of an alloying element to the electrodeposited copper, and among the possible metals, silver can be an attractive option for its high conductivity. This metal, normally immiscible with copper at room temperature, forms a supersaturated alloy when electrodeposited. The main aim of this work is to understand the behavior of this resulting system.

In the sample preparation phase a novel electrolyte based on $CuSO_4$ complexed by $K_4P_2O_7$ and $AgNO_3$ complexed by KI was used for the deposition of CuAg having a range of compositions between 3% and 16% (atomic). The deposition occurred in non- stirred conditions and at 50°C on nickel plated steel.

The XRD analysis of the samples shows a slightly linear shift in the position of the visible peaks; the recorded linear shift is correlated to a constant deformation of the lattice induced by the increasing interstitial silver atoms. This can be visualized representing the difference between the mean (111) interplanar distance of pure copper and the one of the alloys. Annealing the CuAg layer at 400°C leaded to the complete separation of the two metals, as predicted by the phase diagram and visualized by XRD. Another effect of the presence of interstitial Ag is the substantial increase in hardness.

Experimental data will be discussed on the basis of a new modelling frame for electrochemical systems.

Self-organization phenomena during electrodeposition of alloys

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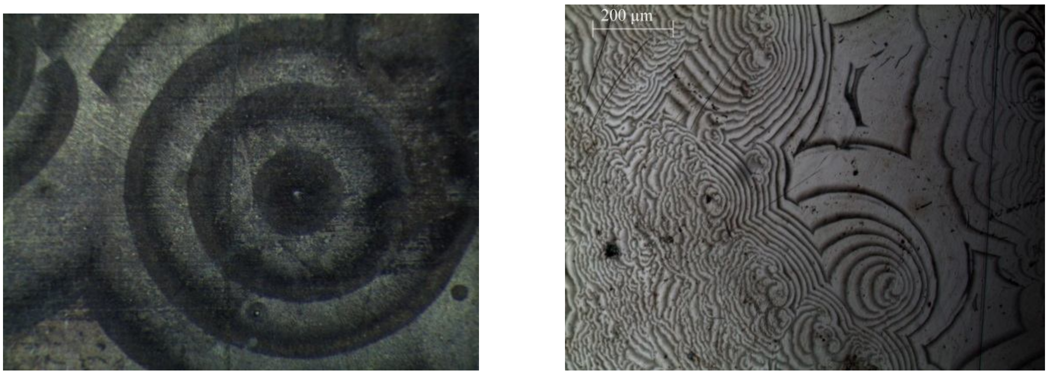
Spatio-temporal structure formation is observed during electrodeposition of some indium coatings, alloyed with silver and cobalt. In these special systems pattern like waves, spirals and targets are formed on the electrode surface during electrodeposition under well-controlled electrochemical conditions – Figure 1a, b. These patterns consist of different phases of the respective alloy.



a) b)

Figure 1. Optical image of electrodeposited alloys: a) Ag-In; b). In-Co alloy

By appropriate combinations of the electrolysis conditions it is possible to observe significant changes in the composition of the coatings leading not only to the formation of spatio-temporal structures on the electrode surface, but also to the achievement of new properties of the alloy coatings.

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Nucleation study of electrodeposited Cu, Bi and CuBi alloys in applied magnetic gradient fields

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Recently it has been demonstrated that structured electrodeposition is possible in applied magnetic gradient fields from electrolytes containing paramagnetic ions. Reverse structured deposits were obtained using electrolytes with strong electrochemical inert paramagnetic ions [1].

In order to understand the first steps of electrodeposition in magnetic field gradients, nucleation studies were performed for metal deposition from paramagnetic and diamagnetic ions without and with addition of strong paramagnetic Mn^{2+} ions on ITO and glassy carbon [2].

The nucleation mechanisms were analyzed electrochemically and the morphology, chemical composition and structure were investigated by SEM, ICP-OES and XRD. Due to the local magnetically induced convection caused by the field gradient force and Lorentz force the nucleation behavior changes and depends from the system investigated. The classical models of Scharifker and Hills are limited since the analysis of the current time transients allows only integral information and don’t consider electrolyte convection near the electrode.

The chemical composition of the CuBi alloy depends on the local magnetic gradient field. In areas of high magnetic gradient field the concentration of Cu is lower than in regions of low magnetic field gradient. This on the first glance unexpected effect i.a. is due to the chosen deposition potential. Cu was deposited in the charge transfer controlled region whereas Bi was deposited mass transfer controlled. The local convection drives the electrolyte with paramagnetic ions in direction of high magnetic gradient fields which enhances the deposition of the mass controlled Bi^{3+} ions whereas Cu deposition is unaffected.

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Modelling and optimization of TiO_2 nanotubes for dye-sensitized solar cells (DSCs)

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Titanium dioxide (TiO_2) is a material with important and distinct properties (semiconductor, photocatalytic, biocompatible, easy to fabricate, stable, non-toxic), that can be used in a wide range of applications, such as sensors, human implants, generation of H_2 by water photoelectrolysis and dye-sensitized solar cells (DSCs) [1,2]. In the particular case of DSCs, the use of TiO_2 material as a photoanode is increasing, due to its advantageous characteristics, comparing with conventional photovoltaic devices. Structures such as TiO_2 nanotubes (NTs) have been investigated for potential improving electron transport and charge separation efficiency [1]. One of the most common and easy ways of producing TiO_2 NTs is by electrochemical anodization techniques. The characteristics of these structures depend on the anodization conditions, such as applied potential and anodization time. So far, the influence of these two parameters in the growing mechanism of the TiO_2 NTs is not completely understood. This understanding is very important to control the anodization conditions and to obtain optimized structures for specific applications.

In this work, we studied the growth mechanism of TiO_2 NTs [particular incidence in the bottom barrier layer thickness (δ_b)], with variable conditions of applied potential (20 – 80V) and anodization time (0.5 – 72h). The δ_b was monitored by STEM (Scanning Transmission Electron Microscopy); the experimental measurements were compared with charge transport. It is established a relation between the anodization voltage with: δ_b, tube diameter, intertube distance and walls thickness.

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Highly-Ordered TiO_2 Nanotube Arrays by Laser Interference Lithography-Guided Anodization

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Self-aligned TiO_2 nanotube arrays (TNA), produced by the inexpensive and flexible electrochemical anodic oxidation method, show a smart combination of tubular geometry and large surface area. Furthermore this nanomaterial is biocompatible and displays many exciting electronic and photochemical properties that can be optimized by adjusting the geometrical parameters of TNA (length, diameter and tube wall thickness) [1]. Thus, many efforts have been made in order to develop novel synthesis strategies that improve uniformity and morphology control of TNA over large surface areas [2].

In this work, we report on a combination of Laser Interference Lithography (LIL) and electrochemical anodization that allows for guiding the growth of TNA. This guided-self organization nanofabrication approach has been recently employed to produce large area, perfectly ordered nanoporous alumina templates of high aspect ratio [3] and it is here adapted to TNA. The Ti substrates are patterned with a regular array of holes by LIL and they are then anodized under controlled electrochemical conditions that allow the well matching between the LIL pattern and the TNA. The morphology, crystalline structure and chemical composition of the resulting TNA were studied by both, scanning and transmission electron microscopy techniques and electron dispersive X-ray spectroscopy, confirming that this combined method allows synthesizing highly hexagonally ordered TNA with amorphous structure and over large surface areas.

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Self-ordered, high aspect ratio and high ordered sub-15 nm porous alumina templates

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Ordered anodic aluminum oxide (AAO) templates with pores <15 nm in diameter and an aspect ratio (length-to-diameter ratio) above 3×10^3 have been fabricated using a nonlithographic approach. Specifically, the aluminum anodization is performed in an ethylene-glycol-water mixture containing sulfuric acid as electrolyte. The effect of the ethylene glycol addition on both the pore diameter and the ordering is evaluated and discussed [1]. Moreover, ordered anodic aluminum oxide templates with pores of 12 nm in diameter and aspect-ratios (length-to-diameter) of > 1000 can also being obtained by lowering the temperature during anodization. Such a low diameter pores are consequence of the reduction of the dielectric constant of the electrolyte together with the effect of increasing the electrolyte viscosity. We show that the temperature has a strong impact on reducing the pore diameter, as provokes the increase of viscosity of the medium and thus the hindering of the diffusion of species involved in the widening of pores. Also, we manage to stop the AAO growth process at the pore nucleation stage and we show that 8 nm in diameter pores are originally formed under these conditions. The presented ultra-narrow pore templates may allow for the preparation of ordered arrays of high aspect-ratio ultra-small one dimensional (1D) nanostructures that could be useful to explore quantum phenomena and integrate quantum-devices [2].

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Advanced metal nanomaterials obtained by refined electroless plating

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Electroless plating is an alternative, wet-chemical route to the electrodeposition of nanomaterials in which electrons are supplied by the autocatalytical decomposition of a chemical reducing agent [1]. Its conformal growth mode favors the fabrication of hollow nanostructures such as metal nanotubes, which are usually obtained within the parallel, cylindrical pores of ion-track etched polymer membranes [2]. Due to the versatility of the technique, the structure of the template and the composition of the plated metal nanofilm can be changed to obtain very interesting and complex nanostructures [3]. This talk will provide insight into some recent developments achieved by our group, including variation of the pore shape, utilization of interconnected pores and direct plating of alloy nanostructures.

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Electrodeposition of thermoelectric Bi_2Te_3 and $(Bi_{1-x}Sb_x)_2Te_3$ nanowires

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Among thermoelectric materials, Bismuth telluride and Bismuth Antimony Telluride compounds exhibit high transport properties at room temperature. Their characteristics are highly dependent on their global composition. In this work, efforts were made to fabricate $(Bi_{1-x}Sb_x)_2Te_3$ nanowires with controllable composition based on an analytical approach. The nanowires were potentiostatically deposited within polycarbonate etched ion-track membranes covered with a platinum substrate. A water/DMSO 50% v/v electrolyte was used in order to improve the filling ratio of the nanopores with Bi_2Te_3 nanowires (from 40 to 80%) [1]. The compositions of the binary and ternary nanowires were adjusted according to the well defined electrochemical deposition parameters [2] and their diameters were controlled by those of the membrane pores. Membranes with 120, 60 and 30 nm pores diameter were prepared from the calibrated etching methods [3], leading to aspect ratio of 1:250, 1:500 and 1:1000 respectively. According to the experimentally determined diffusion coefficients of metallic precursors in the electrolyte and to the analysis of related voltammetric studies, various parameters (applied potential, concentrations of cations) were tested to deposit nanowires

After chemical dissolution of the polycarbonate template, individual characterizations (morphology, cristallinity and composition) were realized by TEM (Transmission Electronic Microscopy) with EDS (Electron Diffraction Spectrometry) analyses. Transport properties of electroplated nanowires were investigated as function of their composition. In particular electrical resistivity and Seebeck coefficient of released individual nanowires were compared with the global performances of arrays of nanowires, acting as thermoelectric generator.

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Electrochemical Optimization of $CoSb_3$ films in DMSO

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In the last decade there has been an increasingly interest in the Skutterudites in the field of thermoelectricity [1]. This interest is based on the fact that the highest performance of this material happens at 400ºC, which makes it ideal for multiple applications as energy harvesting devices. Skutterudites have usually good values of the power factor, but also they offer the possibility of an enhancement of their efficiency due to the reduction of the thermal conductivity via doping the structure or filling of the voids of the structure with heavy atoms. Nevertheless, to obtain the right phase by electrodeposition is still not a solve question. [2]

This work deals the electrodeposition of Skutterudites ($CoSb_3$). We have been able to grow $CoSb_3$ films *via* electrochemical deposition in an organic solvent (DMSO). After studying different parameters such as temperature, stirring, deposition time, potential, heat treatment, lift-off, etc. we have been able to obtain quite homogeneously films with 1:3 ratio.

For the first time, thermoelectric properties of electrodeposited $CoSb_3$ films have been measured in different labs. Seebeck coefficient is determined by to be -12 μV/K in plane and -37 μV/K in out of plane, and an electrical conductivity of around 9 S/cm for in plane.

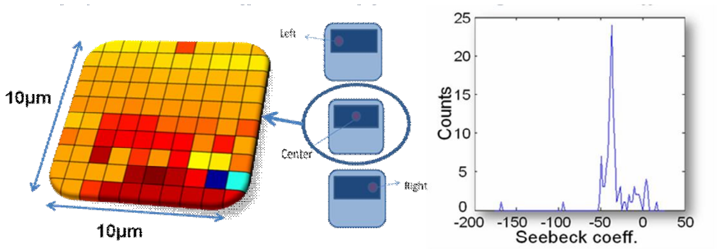

Figure 1 a) 2D map of the Seebeck coefficient out-of-plane and b) Seebeck coefficient distribution

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Thermoelectric power factor of ternary single-crystalline Sb_2Te_3- and Bi_2Te_3-based nanowires

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Nanowires of bismuth antimony telluride and bismuth telluride selenide ($Bi_{15}Sb_{29}Te_{56}$ and $Bi_{38}Te_{55}Se_7$) are grown by template-based pulsed electrodeposition. The composition and the crystallinity of the nanowires are determined by high resolution transmission electron microscopy. The thermoelectric properties (Seebeck coefficient and electrical conductivity) of single p- and n-type nanowires with a diameter of 80 nm and 200 nm, respectively, are determined as a function of temperature before and during heating in helium atmosphere up to 300 K along the growth direction of the nanowires. After additional annealing in Te atmosphere at 525 K, significantly enhanced transport properties are observed. Bulk-like power-factors are achieved. In $Bi_{38}Te_{55}Se_7$ nanowires the Seebeck coefficients increase up to -115 μV K^{-1} and the thermoelectric power factors up to 2820 μW K^{-2} m^{-1} at room temperature. In $Bi_{15}Sb_{29}Te_{56}$ nanowires Seebeck coefficients of up to $S = +156$ μV K^{-1} and power factors of up to 1750 μW K^{-2} m^{-1} are obtained at room temperature.

Reference:
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Electrochemical gating of single molecule junctions using Ni electrodes

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The study of charge transport through single molecule junctions has advanced rapidly over the previous decade, with the ultimate goal of devising electronic devices at the single molecule level. Using the scanning tunnelling microscope break junction technique (STM-BJ) [1], single molecules can be trapped between nano-scopic metal electrodes and their conductance can be measured. We employ the STM-BJ technique under electrochemically controlled conditions to measure the conductance of single molecules contacting Ni and Au electrodes. Electrochemical control ensures clean Ni electrodes which are oxide free; moreover we find that the conductance of the molecular junctions can be changed by varying the electrochemical potential applied to the electrodes. We find that this electrochemical gating effect [2] is significantly enhanced when using Ni compared to Au electrodes, with the conductance of Ni molecular junctions varying by nearly an order of magnitude as the gate potential is changed by only a few hundred millivolts. This demonstrates transistor-like behaviour in single molecule junctions, where the tip and substrate of the STM act as the source and drain electrodes, whilst the gate electrode is provided by the potential applied across the metal-electrolyte interface. The use of Ni electrodes is also of particular interest since it may be possible to construct single molecule spintronic devices when using Ni as the electrode material [3].

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Electrochemical Sizing of Individual Fe_3O_4 Nanoparticles by Anodic and Cathodic Particle Coloumetry

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Magnetite nanoparticles (Fe_3O_4 NPs) find widespread application in medical treatments– both in well-established fields, such as MRI scanning for diagnostics and in perspective therapeutical methods such as hyperthermia. The subsequent distribution within the human body as well as the potential release of these NPs into the environment make their detection and characterisation an important analytical task.

Here we demonstrate that the concept of Anodic Particle Coulometry (APC), an electrochemical method of sizing individual *metal* NPs by oxidizing them upon their impact on an inert micro electrode [1], can be extended to study metal *oxide* NPs, such as Fe_3O_4 (Fig. 1) [2]. Furthermore, a novel route to electrochemical NP sizing is introduced Cathodic Particle Coulometry (CPC). This methodology uses the reduction of impacting NPs, for instance metal oxide NPs, and is demonstrated to yield correct size information for Fe_3O_4 NPs. The combination of these two independent electrochemical methods of NP sizing, allows for solely electrochemical sizing of single nanoparticles and simultaneous verification of the obtained results.

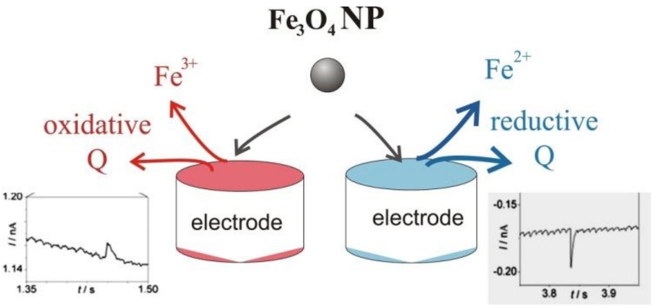

Fig. 1: Schematic drawing showing the principle of nanoparticle impact based sizing of individual magnetite nanoparticles via anodic and cathodic coulometry .

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Formation of Metal Adlayers in Ensemble of Immobilized Nanoparticles.

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Immobilized nanoparticles (NPs) on solid support serve a convenient model of nanodispersed materials. This study analyzes metal transfer between spatially separated NPs of two different metals immobilized on solid support (ITO, glass): Au and Ag, Pd and Ag, or Au and Pd.

Pairs of slides with immobilized citrate-stabilized Au and Pd NPs or bare Ag NPs were brought to contact with each other either under potential control or in the presence of the reduction agent. In-situ LSPR measurements with ITO/Au NP and ITO/Ag NP pair showed fast changes in the surface plasmon bands of both Au and Ag NPs. Electrochemical characterization of NP surface was done using underpotential deposition (UPD) of Pb. After contact with ITO/Ag NP cyclic voltammetry (CV) of Pb UPD on ITO/Au NP electrode was similar to that observed with preformed Au/Ag UPD electrode. This result indicates that Ag monolayer was formed on Au NPs surface. Similarly, after contact with ITO/Ag NP UPD of hydrogen on ITO/Pd electrode was suppressed.

X-ray photoelectron spectroscopy (XPS) revealed substantial transfer of Ag to ITO/Au NP and ITO/Pd NP electrodes. No traces of Au were found on ITO/Ag electrode after contact, while small amount of Ag was transferred to ITO/Pd electrode. In-situ LSPR experiments and XPS analysis of glass/Au NP and glass/Ag NP slides confirmed Ag transfer to Au NP immobilised on glass slide, although kinetics of the process was much slower compare to Au NPs immobilized on ITO.

Based on the results obtained in the study we assume that metal transfer between different phases is common in nanostructured composites and can significantly influence catalytic activity.

Capacitive Properties of Electrodeposited Cobalt Hydroxide in Alkaline Solution

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Supercapacitors are electrochemical systems with extremely high specific capacitance and high power density which fill the gap between the large energy density batteries and the large power density conventional capacitors [1]. Supercapacitors possess energy densities of two orders of magnitude higher than those of conventional capacitors while retaining the same power density [2].

Cobalt hydroxide/oxide-based supercapacitors have an attractively high power density arising from faradaic processes. Though, cyclic stability of the cobalt hydroxide/oxide and its capacitance depend on the reversibility of occurring redox reactions.

This study is focused on investigation of the capacitive behavior of cobalt hydroxide/oxide electrochemically deposited on stainless steel in alkaline electrolyte in relation to its long cyclic stability. The capacitance changes are discussed with respect to the different oxidation states of the cobalt hydroxide/oxides and reversibility of the redox reactions.

A specific integral capacitance of cobalt hydroxide/oxide of 510 Fg^{-1} at 20 mVs^{-1} was attained before cycling. The capacitance of cobalt hydroxide/oxide species was demonstrated to decrease by oxidation of cobalt oxide to higher oxidation states during cycling to more stable and reversible redox systems. Experiments show a decrease in integral capacitance of 43.1%, to 290 Fg^{-1} (20 mVs^{-1}) after 600 cycles which is than stable up to 1000 cycles and a strong increase in reversibility after this cycle number.

Therefore, long cyclic life of this material comprises the conversion of the oxidation reaction towards the increase in reversibility. A constant integral capacitance value achieved after long cycling might be attractive for applications.

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Thursday March 20th, 2014

Seminarraum I

POSTERS

Electrodeposition of Silver-Tin Alloys

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The pattern formation in electrochemical systems has been intensively studied in the past two decades. A wide variety of spatio-temporal structures are observed during electrodeposition of several silver based alloys, such as Ag–In [1], Ag-Sb [2], Ag-Bi [3]. Patterned structures can be observed also during electrodeposition of Ag-Sn alloys from cyanide-pyrophosphate electrolytes [4].

In the present study the attempt was made to obtain spatio-temporal structures during electrodeposition of silver-tin alloys from non-cyanide – thiocyanate pyrophosphate electrolytes. The metal content in the basic electrolyte used, was mainly 3 g/l Ag and 20 g/l Sn.

Figure 1. Spiral structure on the surface of electrodeposited Ag-Sn alloy.

The alloy deposition is of regular type (the silver deposition potential is more positive than that of tin) and with increase of the current density the tin content increases. At tin contents in the deposit of about 45-50 wt. % spatiotemporal structures (waves) can be observed on the electrode surface.

In some cases spirals structures are registered (Figure 1).In this contribution spiral structures are reported for the first time for this alloy system.

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Electrochemical synthesis of iron oxide nanowires

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Iron oxide nanomaterials are among the most used materials in nanotechnology due to their wide variety of potential uses, going from photocathodes in solar cells [1] to biomedical applications, like drug delivery [2], contrast agent [3] and hyperthermia mediators [4].

In this work we present two different routes to synthesize iron oxide nanowires, both based on electrochemical deposition. On one hand, iron nanowires were electrodeposited inside the nanopores of a polycarbonate template and afterwards, thermally oxidized. Following this procedure we have already obtained hematite (α-Fe_2O_3) nanowires. The morphology and magnetic properties of the nanowires strongly depend on the oxidation conditions.

On the other hand, we have electrodeposited iron oxide nanowires inside the nanopores of a polycarbonate membrane by an oxidation reaction of Fe ions present in the electrolyte. In this case, we have already synthesized single-crystal goethite (α-FeOOH) nanowires (figure 1). Measuring the magnetic properties we have observed that the core (antiferromagnetic) and the surface (ferromagnetic) of the nanowires are coupled via exchange bias, which could help to control de properties of the wires for magnetic applications.

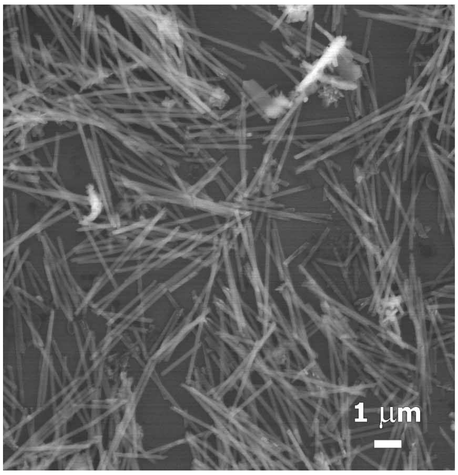

Figure 1. Electrodeposited single crystalline goethite (α-FeOOH) nanowires.

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Electrochemically deposited magnetostrictive FeGa (Galfenol) thin films and nanowires

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Here we report the first measurements of magnetostriction as a function of composition for electrodeposited galfenol. Galfenol is an exciting material due to its large magnetostriction constant (up to 400 ppm) and robust mechanical properties. [1] A wide range of sensors, actuators and other transducers can be fabricated by taking advantage of galfenol's unique mix of magnetic and mechanical properties. We have shown electrodeposition of magnetostrictive galfenol thin films and nanowires.[2,3] Electrodeposition allows galfenol to be easily integrated into a variety of applications, such as toque sensors with conformal, monolithic active layers as well as high aspect ratio nanowires using anodic aluminum oxide templates. In this work, we examine the underlying factors that influence magnetostriction in electrodeposited galfenol, including crystallinity and composition. We have controlled the film composition, as measured by energy dispersive x-ray spectroscopy, over the range of 5-30% gallium using a single plating bath by varying deposition parameters. This composition range corresponds to the region of largest expected magnetostriction for iron gallium alloys. Our electrodeposited films showed polycrystalline texture, as measured using x-ray diffraction. The magnetostriction of these films was measured using the capacitance bridge method as described previously [3]. Our results are within the expected range, when the polycrystallinity of the films is accounted for. These results show that it is possible to achieve large magnetostriction in galfenol using electrodeposition.

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Poster 4

Tailoring electroless plating characteristics for successful nanotube fabrication

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Electroless plating is a versatile wet-chemical route towards the conformal deposition of high-quality metal films. Using templates like ion-track etched polymer membranes in conjunction with this deposition method, intricate metal nanostructures such as high aspect ratio metal nanotubes can be obtained [1-3]. Due to their promising functional properties, these nanostructures are interesting for applications in e.g. catalysis [1,3], sensing [2] or permselective transport [4]. Because the desirable plating reaction characteristics required for industrial metallization of regular work pieces and nanomaterial fabrication vary distinctly, available deposition reactions can often not be applied to micro- or nanostructured templates with challenging morphologies. On the basis of three examples (Ag [1], Rh [2] and Ni [3] plating), it will be shown how the coordination chemistry of the metal precursor aside important reaction parameters can be used to create plating baths suitable for the deposition of well-defined metal nanotubes.

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Poster 5

Influence of magnetic gradient fields on the electrodeposition of Co, Fe and CoFe

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Recently, an electrochemical method of structuring by means of magnetic gradient fields has been introduced for metal deposition [1]. Structuring of magnetic materials in particular CoFe alloys with high saturation magnetization makes this method highly attractive for industrial applications in microelectronics. Therefore the electrodeposition of Co, Fe and CoFe on Au from additive free sulfate based electrolytes has been studied under the influence of magnetic field gradients ($B\nabla B$) .

An electrochemical quartz crystal microbalance was employed to determine the metal current efficiency. The topography, morphology and chemical composition of the metal layers was characterized by profilometry, SEM and EDX. The magnetization behavior was investigated with VSM. The deposited mass and current efficiency increases with rising magnetic field strength due to the field gradient force and the resulting electrolyte convection. Highest layer thicknesses are formed at regions of high $B\nabla B$. The structures developed during deposition depend and correlate with the magnetic properties of the ions and the magnetization of the formed layers, which contribute to $B\nabla B$. The morphology of the deposited layers is varying depending on the local magnetic field gradients caused by complex convection behavior of the electrolyte. The chemical composition of the CoFe layer correlates to the ion ratio of the electrolyte and is constant across the structure. First time it has been demonstrated that this deposition method can be used for alloy patterning [2,3].

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Investigation of the dealloying of electrochemically grown AuAg nanowires

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AuAg-based and porous nanowires are of interest for sensorics, surface plasmon enhanced spectroscopy and catalysis. AuAg materials are very attractive for the analysis of biological media due to their low toxicity and their well-known chemistry. Combined, they are also expected to have an enhanced catalytical activity [1]. For porous wires, their tortuous structures and/or surface roughness are expected to free chemically highly reactive surfaces and to create numerous hot spots of interest for surface enhanced Raman spectroscopy (SERS). In addition, the high surface to volume ratio of the 1D structure may lead to higher sensitivity and/or efficiency of catalytic and sensor devices.

In this work, we investigate the fabrication of smooth, porous and rough AuAg nanowires by electrodeposition in etched ion-track membranes and subsequent Ag dealloying. AuAg nanowires with different compositions are electrochemically deposited from a single-bath electrolyte into the pores of etched ion-track polymer templates fabricated at GSI. By selective Ag dissolution in nitric acid, both rough and porous nanowires are created depending on their initial composition. To obtain a better insight into the Ag dealloying process, composition and crystallographic properties of the nanowires are analysed before and after Ag dissolution. Various methods such as X-ray diffraction, energy dispersive X-ray spectroscopy, and high resolution transmission electron microscopy are applied.

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Electrodeposition of Palladium – Indium alloys

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The properties of electrodeposited palladium-indium alloys are not extensively investigated. We present an attempt to obtain compact coatings in a wide compositional range, in order to investigate their properties. There is scarce information about appropriate electrolytes for Pd-In alloy electrodeposition [1]. Cyclic voltammetry investigations in ammonia-citrate electrolytes show, that the alloy phases are formed at more positive potentials than those of the pure metals. Already at low current densities (0.1-0.2 A dm^{-2}) the coatings contain about 10-18 wt. % of indium. Formation of spatio-temporal structures is observed on the surface of the deposits (Figure 1). The structured coatings contain 10-18 wt. % of indium.

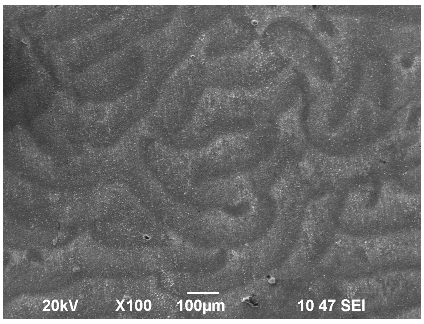

Figure 1. SEM image of electrodeposited Pd-In alloys

The investigations on the phase composition of the coatings with spatio-temporal structures show that they consist from a pure palladium phase and the $Pd_{0.85}In_{0.15}$ – phase. The pattern formation observed on the surface of solid electrodes during electrodeposition of some alloys under well controlled electrochemical conditions is a very attractive and rare phenomenon. The observed pattern are stable with time and the investigated systems could be used as model systems in the investigations of self-organization phenomena.

Acknowledgment: The authors are grateful for the financial support of Project BG051PO001-3.3.06-0038 funded by OP Human Resources Development 2007-2013 of EU Structural Funds.

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Surface modification of etched ion-track templates by atomic layer deposition of SiO_2, Al_2O_3 and TiO_2

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For the application of high aspect ratio nanostructures in catalysis, filtration, and purification the modification of their surface is of great interest. One challenge is still the development of suitable fabrication techniques to precisely tailor their surface properties according to their dimensions. On the way to novel industrial applications systematic studies on these nanostructures are required.

Here we modified the surface of etched ion-track polycarbonate (PC) templates by atomic layer deposition (ALD). 30 µm thick PC foils were irradiated at the GSI linear accelerator UNILAC with ~ GeV heavy ions. Subsequent chemical etching transforms each ion-track into a cylindrical nanochannel with a diameter between 400 and 20 nm, depending on the etching time. Thus the templates exhibit nanochannels with defined aspect ratios between 75 and 1500. In order to functionalize the surface, these templates are coated by ALD with layers of controlled thickness of alumina (Al_2O_3), titania (TiO_2) and silicon dioxide (SiO_2). The homogeneity of the ALD surface modification process inside the nanochannels is studied by various methods. Small angle X-ray scattering is applied to determine average channel diameter and diameter distribution before and after the coating. The surface composition is analysed by X-ray photoelectron spectroscopy. Furthermore, the polymer template is dissolved by wet-chemical methods to characterize the resulting inorganic nanotubes. Scanning electron microscopy (SEM) and scanning transmission electron microscopy in SEM visualize nanotubes with exactly defined diameters and wall thicknesses. Their composition is studied by energy dispersive X-ray spectroscopy, evidencing the homogeneity of the surface modification inside the nanochannels.

Poster 9

Graphene-based electrodes for supercapacitors

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Supercapacitors, also called double layer or electrochemical capacitors or ultracapacitors are devices for electrical energy storage particularly suitable for applications requiring high power density such as energy back-up systems, consumer portable devices and electrical/hybrid automobiles. Recently, electrochemical supercapacitors have become the focus of intensive researches. Carbon-based electrodes are known to be suitable materials to provide electrochemical double-layer capacitance, directly proportional to surface area and pore size distribution.

Although carbon nanotubes electrodes exhibit relatively large surface area (around 200 m^2g^{-1} for MWCNT), high electrical conductivity along the tubes and good capacitance performance, the high cost of manufacturing limits their commercialization.

Graphene is a monolayer of sp^2-bonded carbon atoms with large theoretical surface area (about 2630 m^2g^{-1}) and high intrinsic in-plane electrical conductivity. Graphene oxide synthesized by the modified Hummers method contains oxygen functional groups on the surface which can be removed by means of different methods: chemical reduction (hydrazine, sodium borohydride), electrochemical cyclic voltammetry and thermal treatment.

In the present work we describe a novel procedure for the fabrication of electrodes for supercapacitors application. Graphene oxide nanoplatelets were obtained following the modified Hummer's method. As-synthesized graphene oxide was deposited onto a conductive substrate (titanium mesh, stainless steel mesh, nickel) by electrophoretic deposition. As second step, a thermal treatment in reductive atmosphere (made by H_2 and N_2) was carried out in order to remove the oxygen functional groups from graphene oxide, partially restoring the pristine sp^2-lattice of graphene. Electrochemical characterization of the electrodes was carried out in aqueous electrolyte (1M Na_2SO_4 and 6M KOH) as well as in organic commercial solutions.

Results obtained at room temperature and 10 mV s^{-1} of scan rate show a specific capacitance of 131 F g^{-1}, 98 F g^{-1}, and 167 F g^{-1} using Titanium, AISI 316 L or Ni meshes, respectively. It has been found that electrodes increase their performance while cycling: the specific capacitance increased up to 67% compared to the initial value after 2000 cycles. This might be attributed to further electrochemical reduction of residual the functional groups on the graphene platelets.

Finally it has been found that an overloading of graphene oxide onto the metallic current collector does not lead to higher capacitance.

Poster 10

Improving methanol oxidation activity of metal nanotubes by exchange and dealloying chemistry

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Direct alcohol fuel cell (DAFC) technology is one promising technology to generate energy for e.g. transportation or mobile electronic devices. Currently the majority of commercial DAFC cathode electro catalysts are based upon carbon-supported platinum nanoparticles. The use of expensive platinum is one of the main obstacles to overcome when making DAFCs attractive to industrial usage. Current approaches to improve the platinum utilization include using one-dimensional nanostructures [1] with a high surface-to-volume ratio or improving the catalyst activity by alloy formation [2]. Both approaches are combined in this work. First, silver nanotubes are fabricated by electroless plating [3], which are consequently alloyed with platinum using simple exchange chemistry [4]. Remnant silver can be selectively removed, to tune the metal ratio of the alloy nanotubes. Due to the distinct impact of the composition on the catalytic properties, this set of reactions can be used to optimize the nanotube catalysts. Tailored nanotubes significantly outperform the specific activity of commercially available, carbon-supported platinum nanoparticles.

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Poster 11

Development of Pt Bimetallic Electrocatalysts Using Electrochemical Methods

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Platinum (Pt) is very active fuel cell catalyst, but its cost is still high to be used commercially. Scientists in the field of electrocatalysis are working on development of various catalysts with lower amount of Pt, while maximising their catalytic activity. Development of bimetallic Pt surfaces is one of many approaches actively explored at the moment to achieve this. Many studies showed that nanoscale Pt such as Pt ultrathin layers, and clusters on different substrates X and PtX nano-alloys have different chemical and physical properties than those of Pt bulk [1-3]. These different bimetallic systems have low Pt content but they have high activity due to the combination of electronic and geometric configurations. The designing of Pt clusters on different substrates using electrodeposition processes has attracted attention from electrocatalysis and electrodeposition community. In this work we explore electrochemical methods for design and controlled coverage of Pt clusters on Gold (Au). Because standard Pt electrodeposition at constant potential on Au produces incomplete three dimensional films [4], a method known as Surface Limited Redox Replacement (SLRR) has been developed [5,6]. In this method an underpotentialy deposited (UPD) layer of less noble metal, like Cu or Pb, used as sacrificial layer is galvanically replaced by Pt at an open circuit potential (OCP). Following recent work of our group of growing two dimensional Pt films using SLRR via Pb UPD6 we explored conditions for controlled growth of Pt clusters on Au. The amount of Pt deposited was controlled by Pb sacrificial coverage as a function of the underpotential applied. The study of Pb UPD on Au (111) isotherm and its use for Pt cluster deposition as a function of Pb UPD coverage will be presented. The electrochemical behavior of created bimetallic Pt-Au surfaces will be analyzed as a function of Pt versus Au surface coverage.

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Poster 12

Magnetic anisotropy in electrodeposited Ni-Co-Fe ternary alloy nanostructures- Towards applications for high density information storage

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Magnetic multilayers are fabricated on evaporated gold substrates by pulsed electrodeposition. Alternating layers of high magnetic moment Ni-Co-Fe alloy (FM)[1,2] and a non-magnetic Cu spacer (NM) are deposited by modulating the potential (E) at the working electrode between E_{FM} and E_{NM}.[3] Furthermore, induced magnetic anisotropy has been observed in these films when an external magnetic field of 500 Oe is applied during growth. The magnetic properties of these films are characterised with a vibrating sample magnetometer (VSM) and the structural properties with inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and x-ray diffraction (XRD). The magnitude of anisotropy (H_k), coercivity (H_C) and alloy composition are studied as function of the electrochemical parameters (electrode potential/ current density) and the individual layer thickness. The observation of induced anisotropy and tuneable coercivity in thin film multilayers is significant because it presents opportunities for novel information storage and logic routines by programmable easy axis direction and exchange coupling between successive layers4,5.

Electrodeposited multi-layered magnetic nanowires are also of interest, where the deposition of the desired species occurs through a nanoporous polymer membrane[6]. Track-etched polycarbonate membranes have been selected because they are commercially available with a convenient range of pore diameters (15-100nm) and the membranes and are hydrophilic which allows wetting of the solution through the pores. Field dependent transport experiments to measure the giant magnetoresistance (GMR) of these nanowires will be performed both with a macroscopic probe and conductive-probe AFM. Magnetic nanowires are an attractive candidate for next generation information storage as ordered arrays of single domain information carriers[7]. Studies of induced in-plane anisotropy in multilayer films will be applied to multi-layered nanowires.

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Poster 13

Anodic iron oxide nanotubes: structural and magnetic characterization

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Highly-ordered hematite (α-Fe_2O_3) nanotubes (NTs) have gained relevance for application in hydrogen production by water splitting (photoelectrochemical cells) [1] due to its narrow band gap about 2.0-2.2 eV, which collects up to 40% of the solar spectrum energy. However, the hematite materials have poor electron mobility that results into high electron-hole recombination rate and, short hole diffusion length. In order to overcome these drawbacks, nanostructuring techniques have been proven useful for increasing the performance of the hematite's photoresponse [2]. Boost of optimized and fast routes of α-Fe_2O_3 NTs production are of pivotal concern.

In this work, we synthesized iron oxide NTs starting from an iron foil in fluoride containing electrolytes via an electrochemical anodization method. The NTs' geometry depend on different anodizing parameters (electrolyte type, concentration, pH, time, temperature and applied potential) that determine the relevant tube features (length, pore diameter and wall thickness). Fast-growth of iron NTs arrays were obtained with an anodization potential of 50 V in an ethylene glycol solution containing NH_4F (0.5 wt%) and H_2O (2 wt%) at 45^oC [3,4]. Through scanning electron microscopy (SEM) it was determined the NTs morphology, unveiling NTs features, diameter and length. Afterwards, the as-prepared NT samples were annealed under different conditions, time and temperature, in an oxygen atmosphere in order to obtain crystalline iron oxide NTs. It was observed that after 1h the iron oxide NTs start to crystallize at temperatures above 400^oC. The X-ray diffraction spectrum discloses that 2 iron oxide phases are always present: magnetite (Fe_3O_4) and α-Fe_2O_3. These achievements were further corroborated by the temperature dependence of magnetization measurements, namely by the presence of a breakdown of magnetization magnitude at T_V~120 K, arising from the electronic transition of Fe_3O_4 (Verwey transition). Additionally, and one anomaly at T_M ~190 K is also presented due to the antiferromagnetic spin flop transition of the α-Fe_2O_3 (Morin transition). The isothermal hysteresis loop proves that all the oxide NTs are ferromagnetic at room temperature with coercive fields ~ 150 Oe and up to 400 Oe for low temperatures.

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Magnetic-lipid nanoparticles using electrodeposited nanowires

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Magnetic nanowires have attracted considerable attention as a multimodal generation of nanocarriers that can be used for targeted drug delivery and that combined with hyperthermia can thereby improve the therapeutic index. A well-known self-organized template to grow nanowires is porous anodic alumina (PAA) [1], as it allows the low-cost and high-yield growth of highly ordered nanomagnet arrays.

This work describes the synthesis and characterization of ordered arrays of nickel nanowires (NWs) with tunable small lengths (< 100 nm) obtained by potentiostatic electrodepositon of Cu/Ni multisegments in a PAA template with ≈ 50 nm of pore diameter. The main advantage of this electrodeposition method is the possibility to deposit sequentially different materials inside the template pores using a single electrolytic bath and yielding segmented nanowires of different materials [2]. Also, by changing the deposition time and applied potential, we are able to control the wires length, allowing us to study Ni segments with different lengths.

The structural study of the obtained Ni/Cu NWs evidenced the existence of Ni and Cu layers with a polycrystalline structure. In order to study the influence of the size of the Ni NWs on their magnetic properties, magnetization as a function of the applied field was measured. The coercivity as a function of the NWs length shows that for arrays of NWs with high-aspect ratio, the coercivity increases with the NWs length indicating that the shape anisotropy prevails, and the magnetization aligns along the longitudinal axis of the NWs. For samples with low-aspect ratio, we have an opposite behavior were interwire coupling may overcome shape anisotropy. In this work, we have also dispersed the magnetic Ni NWs obtained with length from 10 to 100 nm and encapsulated them in a lipidic shell, to obtain biocompatible particles. We show that, even with the lipidic shell, the magnetic behavior of the nanoparticles remains. Toxicity and compatibility studies have also been performed in *in vitro*.

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Electrodeposition, structural analysis and magnetic properties of Co-Bi multilayers

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The Co/Bi system offers new effects to be studied in layered form due to the magnetic/semimetal interfaces. Especially interesting can be the giant magnetoresistance (GMR) in Co/Bi multilayer films and multilayered nanowires. Up to now, Co/Bi multilayers have only been prepared by physical deposition methods (e.g., sputtering). The reason for this fact is due to the significant difference in standard potential values of the two elements ($E_{\mathrm{Co}} =$ -0.28 V and $E_{\mathrm{Bi}}=$ +0.32 V). Furthermore, the phase diagram of Co-Bi system shows no miscibility at room temperature.

It is always important to compare various fabrication methods. This is particularly important for nanowire systems where electrodeposition is much more suitable than any other preparation method. Electrodeposition offers a relatively simple and inexpensive preparation technique for such multilayers as compared to physical deposition methods, and nanowires can be produced only with the help of electrochemical deposition.

The current work is focused on the preparation of Co/Bi multilayers by using an electrochemical preparation technique. The structure of the deposits was investigated by scanning electron microscopy, atomic force microscopy and X-ray diffraction. The optimization of the parameters of the electrodeposition bath and a structural analysis of the deposited Co/Bi multilayers will be described. Furthermore, an investigation of the layer thickness dependence of the magnetoresistance and other magnetic properties will be presented.

Poster 16

Near-substrate composition depth profile of d.c.-plated and pulse-plated Fe-Ni alloys

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Electrodeposition is a widely used technique to produce Fe-Ni alloys. The importance of the Fe-Ni alloys stems mainly from their magnetic properties, especially the low coercivity. The first review of this topic was published as early as in 1962 [1]. Fe-Ni plating can be classified as anomalous codeposition.

In the present work, the composition depth profiles of d.c.-plated and pulse-plated Fe-Ni samples have been measured with secondary neutral mass spectrometry. The composition depth profile measurements were carried out in the so-called reverse mode [2] when the deposit was peeled off from the substrate and the sputtering process started at the substrate side. Therefore, the composition profile of the near-substrate zone of the deposits could be measured with a high efficiency. It has been found that the molar fraction of iron near the substrate is higher than during the steady-state deposition when d.c. plating is applied. The steady-state composition was achieved typically after depositing a 90-nm-thick alloy layer. In the pulse-plating mode, samples with nearly even composition could be obtained at a duty cycle of 0.2 or smaller, and a continuous change in the composition profile could be seen as a function of the duty cycle above this value. For obtaining deposits of small thickness ($d < 200$ nm) with even composition, pulse plating must be preferred to d.c. plating. The composition depth profile was also measured for a wide range of Fe^{2+} ion concentration in the bath. The different characters of the composition depth profile as a function of the deposition mode can be explained mostly with mass transport effects. The composition gradient formed during the d.c. plating may have a significant impact on the residual stress in the deposit, which may also lead to an increase in the coercive field of the samples. The results achieved help us to elaborate deposition conditions of ultrathin magnetic samples with even composition along the thickness [3].

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Poster 17

Photoelectrodeposition of conducting polymers onto inorganic semiconductor nanoarchitectures

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The number of scientific studies on hybrid materials consisting of conducting polymers (CPs) and ordered metal oxide semiconductor (O_MOS) nanostructures is in a constant rise. The cause of this emphasized attention is the potential applications of these materials in next generation electronics such as high-efficiency solar and fuel cells, batteries, and supercapacitors. These hybrids are usually assembled by filling the O_MOS framework with CPs through different methods. However, in the case of solar cell applications it is necessary to involve a third component to enhance light absorption and to promote charge transfer between the MOS and the CP. These so called "sensitizers" can be organic dyes, metal-chalcogenide quantum dots, and perovskite compounds.

O_MOS nanostructures used as the framework material of the above-mentioned devices offer several key virtues, such as high surface area, porosity, and unique 1D electronic transport. In our work, we apply a versatile method to fabricate such nanostructures, namely the electrochemical anodization of the respective metal foil (Ti, W, Nb), in the presence of a complexing agent (mostly F^-). This way through the deliberate variation of the anodization parameters (solution composition, applied bias voltage) nanoporous or even nanotubular structures can be obtained, which maintain electric contact with the supporting metal electrode. The binding of the sensitizer to the nanostructures is achieved through hydrothermal synthesis (metal-chalcogenides) and sequential or direct deposition (perovskite compounds). The synthesis conditions affect both the loading quantity and quality of the nanostructures, which have a strong impact on the efficiency of the formed composite materials. The CP is then *in situ* deposited on this decorated surface by electrochemical and photoelectrochemical methods.

In this work we present our recent findings on the synthesis and application of these ternary composite materials, with particular regard to solar energy conversion.

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Poster 18

Electrodeposition of Bi_2Te_3 Nanomaterials for Thermoelectric Generators

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The development of innovative energy generators for low power devices with advantage of being portable is probably one of the main challenges nowadays. This quest can be overcome by developing innovative micro/nanogenerators throught the scavenging of energy – the so called Energy harvesting. Thermoelectric (TE) based devices appears as an alternative solution for wast energy since there is several waste heat sources in worldwide (furnace, solar, etc.) and even the heat released by human body [1].

Furthermore, TE nanomaterials reveal that can tune the Figure of Merit (ZT) and overcome the limit of ZT of 1 at room temperature, which was the limit observed during last decades in bulk materials. Electrodeposition appears as a good alternative to produce these TE nanomaterials since it is a low cost method and can produce easily high yields of materials.

In this work, we will discuss two types of nanomaterials of Bi_2Te_3 by DC electrodeposition technique: a) Thin films of Bi_2Te_3 and b) Nanowires of Bi_2Te_3 assisted by Nanporous Alumina template.

From X-ray diffraction we observed that our nanomaterials are crystalline presenting the crystallographic structure expected to Bi_2Te_3. Scanning Electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy reveal that morphological, our samples present a cluster-like shape and that by changing the applied tension we can tailor the Bi/Te ratio. This last point it is very important in order to choose the type of semiconductor (p or n) and thus tuning the figure of merit of the nanomaterials. Finally, the transport properties will be presented.

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Poster 19

Bi_2Te_3 nanowires electrodeposited in etched ion-track templates: Structural characterization and magneto-transport measurements

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We synthesize and investigate nanowires of Bi_2Te_3, known as thermoelectric and topological insulator material. Etched ion-track polymer templates with cylindrical channels of diameters between 20 and 75 nm, and length of 30 μm were fabricated by heavy ion irradiation and selective chemical etching of the ion tracks. By subsequent electrodeposition of Bi_2Te_3 in the channels, nanowires of these geometries were fabricated. The chemical composition and crystallographic structure of the obtained Bi_2Te_3 nanowires are analyzed by means of high resolution scanning electron microscopy (HRSEM), energy dispersive x-ray spectroscopy (EDX), transmission electron microscopy (TEM) and x-ray diffraction (XRD) [1,2].

Bi_2Te_3 nanowires were transferred onto a silicon substrate and contacted by laser scanning as well as by electron beam lithography. The devices exhibit a resistivity of the order of 1.0-1.2 mΩcm at room temperature with negligible contribution of the contacts. The magneto-transport properties were investigated at low temperature (2 K) under pulsed magnetic field of up to 55 T applied parallel and perpendicular to the wire axes. In the large diameter nanowires, the smooth and positive magneto-resistance suggests diffusive transport of the charge carriers without clear signature of the contribution of surface states. On the other hand, clear and reproducible magneto-resistance features show up in small diameter nanowires, which origin is still under investigation. Additionally, these transport measurements allow us to further characterize mobility and carrier density in the electrodeposited Bi_2Te_3 nanowires as a function of wire diameter and temperature.

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Poster 20

Electrodeposition of amorphous NiP alloys for application in neutron beam guides

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Deposition of amorphous Ni-P alloys by means of both electrolytic and electroless technique is widespread since the mid 1940's. The application of such amorphous coatings ranges from corrosion resistant protecting layers to non-textured underlayers for other highly demanding surface treatments.

Our present work aims at the deposition of coatings with an unusually high thickness (i.e., up to 200 μm). The NiP coatings have to be deposited onto Al surface. After the formation of the NiP layer, a polishing procedure has to be carried out for obtaining a smooth surface at virtually the atomic scale. The final coating of the specimens is carried out with sputtering in order to obtain a neutron beam guide supermirror.

The poster will present the features of the electrodeposition procedure that are markedly different from those applied in the usual thickness range, with special emphasis on the result achieved to obtain thick deposits with a low surface roughness.

Poster 21

Impedancemetry as a Tool to Investigate the Variation of Electrical Properties in Gas-Sensor Tin Dioxide Nanowire Mats

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The layers of nanocrystaline oxide semiconductors are of high interest for different applications as far as the reduction of crystal dimensions to nanoscale allows one increasing surface effects on the crystal electric properties. It makes these structures extremely attractive in particular for gas-sensing devices. To increase the gas response selectivity, the layers might be segmented by multiple electrodes to build a sensor array whose vector signal is processed by pattern recognition algorithms. Previously we found that SnO_2 nanowires are very promising material for these applications [1]. Though, these studies were limited by dc measurements while application of impedance spectroscopy [2], which was mostly employed to characterize electrochemical systems, ceramic materials, offers new opportunities for increasing the dimensionality of gas sensing.

Here, we study by impedance spectrometry the SnO_2 nanowire mat placed over $SiO_2/Si/SiO_2$ substrate equipped with multiple coplanar electrodes. The electrical response of each sensor segment located between a pair of electrodes in the multielectrode chip has been recorded under various gases at variable concentrations in mixture with air. Nyquist plots recorded for each segment exhibited two semicircles which can be associated with RC components of equivalent circuit. For the lower frequencies we expect CPE element to describe it best. This is the most sensitive component to gas type and concentration and can be related to capacitance/diffusion elements of equivalent circuit. Each component or their combination can be used for gas identification since there is no correlation between the components. All the components of the circuit depend not only on the gas but also on the gas concentration. Thus, one can employ a pattern recognition algorithm like Linear Discriminant Analysis (LDA) and selectively determine the gas traces in air.

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Poster 22

Magnetic Anisotropy in electrodeposited CoCu Nanowire Arrays

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Co-based alloys have been extensively studied due to the characteristic *hcp* crystalline structure of Co, which introduces specific magneto-crystalline anisotropy providing interesting physical properties [1, 2]. This structure can also be conveniently modified by alloying and/or adjusting the fabrication parameters for tuning a particular property in order to fabricate novel functional materials. In this work Co_xCu_{1-x} nanowires have been electrochemically deposited into the pores of Anodic Alumina Membranes used as templates. The nanowires have been electrodeposited from a Co-Watts type electrolyte containing $CuSO_4$ as Cu^{2+} ions source. The Cu content of the alloy has been adjusted by controlling the deposition potential. The microstructure and composition of both, membranes and nanowires, was determined using a Scanning Electron Microscope equipped with an Energy Dispersive X-ray microanalysis system. The crystalline structure of the nanowires has been carefully study by X-Ray Diffraction and High Resolution Transmission Electron microscopy. Finally, the magnetic properties of the nanowire arrays as a function of the applied magnetic field as well as the temperature have been measured by Vibrating Sample Magnetometry. As a result, even for Cu additions as small as 8 at. %, the crystalline structure of the nanowires is modified, favoring a CoCu *fcc*-phase. This results in the decrease of the magneto-crystalline anisotropy becoming in a magnetic behavior guided by shape anisotropy. Furthermore, and unexpected increase of the coercive field as the temperature is increased has been observed, and correlated to the magneto-elastic nature of Co and the stresses between nanowires and alumina template [3].

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Photoactive Titanium dioxide layers obtained by low temperature plasma electrolytic oxidation

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Plasma Electrolytic Oxidation (PEO) has been known since long time as an industrial method for producing oxidized layers on metals, particularly Al, Mg and Ti alloys, mainly with the aim of increasing surface hardness and wear resistance. More recently, the PEO process was also proposed as an effective route to obtain photoactive porous crystalline titanium dioxide layers. However, the investigation of PEO of commercially pure titanium substrates mainly report difficulties in controlling the phase composition of the coating, and therefore its photoactivity.

In the present study, low temperature PEO of Titanium is proposed as a novel approach to obtain crystalline nanoporous photoactive TiO_2 coatings. Oxidation of Grade 1 Titanium substrates was carried out at 160 V in 0.5 M H_2SO_4 for processing times ranging from 5 to 20 minutes. The PEO process was carried out at temperatures in the range 20 to -3.5°C. Nanoporous crystalline coatings were obtained, consisting in a mixture of anatase and rutile phases. Phase composition did not significantly vary with processing time, expecially at low temperature. On the other hand, by decreasing the processing temperature from 20°C to -3,5°C, an increase of the weight fraction of anatase from 28 to 93% was observed. Correspondingly, the photoactivity of the PEO coatings, as assessed by linear sweep voltammetry under UV irradiation at λ=254 nm, was higher than the photoactivity of commercially available anatase-rich nanotubular TiO_2 coatings taken as a reference. The scalability of the proposed approach was demonstrated by preparing a large area photoactive electrode (540 cm2). The electrode was integrated in a laboratory-scale reactor and the decolorization of an recalcitrant organic azo-dye was tested.

Influence of electrodeposition conditions on the morphology and magnetic properties of CoFeB/Sn multilayered nanowires

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Ferromagnetic nanowire arrays present great interest due to their potential applications as high density magnetic recording media and magnetoresistive sensors. Electrodeposition into nanoporous membranes is an efficient low-cost method for the fabrication of high quality multilayered nanowires.

In this paper we present some results on the preparation and characterization of electrochemically deposited [CoFeB/Sn] x n multilayered nanowires. Systematic studies have been carried out in order to obtain the softest magnetic materials, by varying the composition, the potential value and the ton/toff ratio of the pulsed deposition potential. The optimized conditions which yielded to the smallest in-plane coercivity, Hc = 9.9 Oe, for the electrodeposited thin films were used for the electrodeposition of the nanowires.

The nanowires were deposited in commercially available Whatman alumina membranes, with thicknesses of 60 μm. Sn constitutes a less expensive alternative for the use of nonmagnetic metals in the specific electrodeposition bath, due to its negative reduction potential and still sufficiently more positive than the one for Co and Fe in order not to co-deposit, and it was used in our study for the fabrication of multilayered nanowires.

SEM images show a very good uniformity of the nanowires inside the membrane. The thickness of the layers can be adjusted by the deposition time, multilayered nanowires of 50 μm in length being obtained, with sequences of CoFeB layers (100 nm, 70 nm, 50 nm) and Sn layers (30 nm, 20 nm, 10 nm). VSM measurements revealed in-plane coercivities up to 75 Oe, much larger than the ones obtained for the similar thin film structures. The reason for such a behavior is not fully understood, and it can be ascribed to the magnetostatic interactions between nanowires in the array. The orientation of the easy axis is determined by the competition between shape and magnetocrystalline anisotropies, as well as by the ferromagnetic and nonmagnetic layers aspect ratio (length/diameter) through dipolar interactions, revealing tunable magnetic properties for desirable applications.

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Poster 25

Electrodeposited zinc-ceria nanocomposite coatings: TEM-scale characterisation and properties evaluation

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Protection of steel against corrosion requires the development of more resistant surface treatments in order to enhance the durability of structures exposed to aggressive media. Electrodeposition of new multifunctional composite coatings is a way to achieve this objective [1]. This work deals with the improvement of zinc electrodeposited sacrificial coatings which is not by far the most studied metallic matrix in the field of electrodeposited composite coatings. The objective is to determine the influence of the introduction of ceria nanoparticles into zinc coatings on their functional properties (corrosion resistance, mechanical properties).

Bath formulation (pH, surfactants) was optimized through a preliminary study focused on the zeta potential of ceria nanoparticles in different electrolytes, to get a codeposition of uniformly distributed particles into the zinc matrix. Nanocomposite coatings were elaborated using direct current [2].

Coatings were then characterised adopting a metallurgical approach: micro-hardness measurements, SEM observation and XRD analysis. GDEOS profiles and TEM analysis of FIB- and ultramicrotomy-cut samples were also conducted to study the distribution of the nanoparticles through the coating thickness.

Corrosion behaviour was also determined at both laboratory and industrial scales through a measurement of the electrochemical parameters and the determination of the resistance to salt spray test.

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Poster 26

Characterization of $Bi_{1-x}Sb_x$ nanowires fabricated by electrochemical deposition in etched ion track membranes

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$Bi_{1-x}Sb_x$ ($0<x<1$) nanowire arrays were grown by electrochemical deposition in ion-track etched membranes. The templates are fabricated by irradiating polycarbonate foils with swift heavy ions (*E* ~ GeV) at the UNILAC, linear accelerator at GSI. On their way through the foil, the ions create cylindrical damage trails that can be converted into nanochannels by chemical etching. By using 6 mol/L sodium hydroxide solution at 50°C [1] as etchant, we fabricated 30-µm thick membranes with parallel cylindrical pores with diameter ~ 15, ~ 30, and ~ 80 nm. $Bi_{1-x}Sb_x$ nanowires are then synthesized by means of both potentiostatic [2] and pulsed electrochemical deposition. X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) images give evidence of the polycrystalline structure of such nanowires.

Nanowires with diameter as small as 15-20 nm are excellent model systems to investigate the predicted enhancement of the thermoelectric figure-of-merit of nanostructures [3, 4]. We are thus testing a special setup to measure the Seebeck coefficient of nanowire arrays embedded in the polymer membrane.

Moreover, to understand possible applications of $Bi_{1-x}Sb_x$ nanowires in thermoelectric systems, their thermal behavior has to be understood. We therefore released our $Bi_{1-x}Sb_x$ nanowires from the matrix by removing the polymer in a suitable organic solvent and transferred the wires both onto thick silicon substrate and thin carbon coated TEM grids. The nanowires on both substrates were thermally annealed at various temperatures in air for 2, 20, and 100 hours. Morphology and composition of the nanowires were studied by both SEM and TEM before and after the annealing process.

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The Electrochemistry Behind the Deposition of Metallic Nanowire Arrays in Thin Pores

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Electronic Packaging is currently deeply in need of new solutions concerning vertical interconnection strategies. With respect to downscaling the geometrical limits, entering the nanoscale for first-level interconnects is nothing more than a consequence. We propose a new strategy for highly resolved vertical interconnects that are realized by metallic nanowires (NWs). Their embedment inside a dielectric matrix enables the further raster size reduction for chip interconnects. Since a maximum number of NWs will be realizing the interconnection quality, the homogeneity in NW length as well as the electrical properties are key parameters for the validation of technological feasibility. Therein the creation of NW arrays is conducted in self-ordering templates (anodized Al_2O_3, AAO) by electrochemical deposition of Ag and/or Ni inside the pores.[1,2] Electrical properties were shown to be sensitive to the mode of deposition. Consequently, there is a direct connection between deposition mechanism and resulting properties of single NWs and the homogeneity of whole arrays, respectively. The overall process was in the past described as diffusively controlled, but this assertion was not further evaluated. The presence of a gradient in the diffusion coefficient as well as the presence and expansion of an electrochemical double layer located at the template's inner surface are responsible for limiting the deposition process. An existing model for porous electrodes by DeLevie[3] is compared to the measured data of electrochemical impedance spectroscopy and found not to be valid for the system of highly recessed ultramicroelectrode arrays by which this system is described. Therefore a new model is proposed that exchanges the inactive capacitive role of the AAO by the active kinetic hindrance which is expressed by a constant phase element. This enables the differentiation between charge-transfer and diffusive motion. A non-linear behavior in the electrode's surface capacitance finally reveals the complex nature of AAO pore deposition.

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