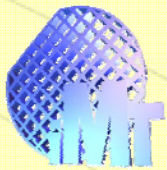




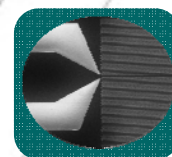
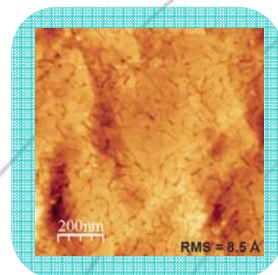
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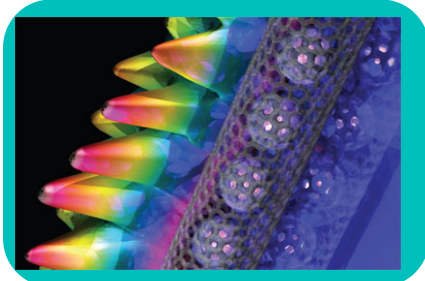


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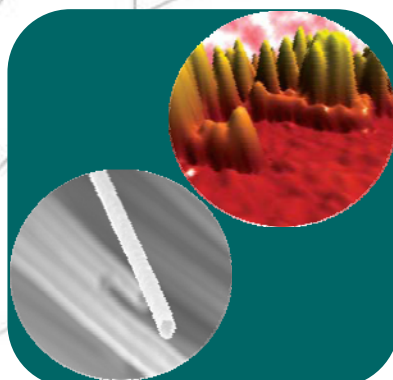
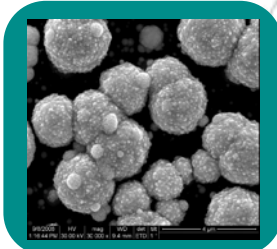


A 10-a editie a Seminarului National de nanostiinta si nanotehnologie



18 mai 2011

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O perspectiva biomedicala asupra Nanotehnologiilor

Dr. biochim. Radu Albulescu

Institutul National de Cercetare Dezvoltare Chimico Farmaceutica

Nanotehnologiile – privite ca forma “fizica” de exprimare a nanostiintelor, reprezinta sectiunea “nano” cu maximum de impact farmacologic si toxicologic. Influentele sunt bidirectionale, produsele nanotehnologiilor fiind unul din subiectele fierbinti ale reglementarilor si investigatiilor in domeniul toxicologic, indiferit de autilizarea intentionata. Procesarea la nivel nanometric modifica considerabil proprietatile biologice, generand schimbari ale reactivitatii chimice, biodisponibilitatii ori capacitatii de interactie cu sistemele biologice. In pofida unor voci critice, reglementarile “particularizate” privind metodologia de testare a nanomaterialelor, ca si dezvoltarea si validarea unor metode adecvate, au condus la emergenta unui domeniu specific, nanotoxicologia. Aceasta poate beneficia de experienta acumulata in toxicologie (indeosebi in cercetarea farmaceutica), importand si adaptand “instrumente” a screeningul “in vitro”, modelarea si simularea “in silico”, biostatistica, biologia sistemelor.

Un segment important al nanostiintelor se orienteaza catre domeniul biomedical si farmaceutic, prin aplicatii destinate diagnosticului si terapiilor avansate, si par sa prefigureze instrumentele de atac pentru rezolvarea unor probleme medico-sociale inaccesibile altor mijloace terapeutice. In ultimii ani, a aparut un spectru larg de aplicatii pentru cercetarea biomedicala si de asemenea, diverse sisteme de diagnostic au ajuns in faze avansate de validare, oferind un camp interesant de dezvoltare, in diagnosticul de laborator (nanosfere activate, noile generatii de dispozitive de inscripționare a “microarrays”), diagnostic in vivo si chiar terapie (quantum dots, nanocapsule si nanoparticule pentru transport si eliberare dirijata).

Este destul de bine documentata capacitatea materialelor de dimensiuni nanometrice de a interfera cu functiile celulare prin facilitarea fenomenelor de stress oxidativ, dar si abilitatea acestora de a modifica reactivitatea celulelor expuse. Trei modele experimentale au fost aplicate pentru estimarea modificarii reactivitatii la citokine: in culturi de limfocite umane s-a putut estima productia de citokine ca urmare a expunerilor toxice, in timp ce in culturi de celule endoteliale umane si in culturi de fibroblaste s-a masurat modificarea raspunsului la citokine pro-apoptotice. Exemplul ofera si imaginea “interventiei” tehnologiilor nano in toxicologie, prin utilizarea unui sistem de multiplexare “liquid array” ce utilizeaza nanosfere fluorescente pentru captura si analitilor. Frontiera nanostiinte – biostiinte pare sa functioneze ca o membrana cu transport bidimensional, cu un potential exceptional de a contribui la realizarea de materiale si aplicatii de mare impact, ce se pot concretiza in accelerarea descoperirilor stiintifice si in noi mijloace terapeutice si de diagnostic.



Nanoworld Telepresence

¹Ioan BURDA, ¹Simion SIMON, ^{1,2}Octavian POPESCU, *opopescu.ubbcluj@gmail.com*

¹*Babeş-Bolyai University, Interdisciplinary Research Institute on Bio-Nano-Sciences, Cluj-Napoca, Romania*

²*Romanian Academy, Institute of Biology Bucharest, Bucharest, Romania*

The absolute goal for biology is the knowledge of molecular, subcellular, cellular and multicellular systems in terms of quantitative models that are supported by the accurate principles of the physical sciences and mathematics. Currently, biology could be defined as the science of nanostructures.

Manipulating and controlling things on a nanometer scale is still difficult. Handling nanoscale objects involves finding these objects, tracking and moving them. The most important line of investigation towards nanomanipulation is nanotelerobotics, where the nanoworld is translated into virtual reality that allows us to interact with smallest objects.

Virtual instrumentation has grown significantly since its inception in the late 1970s and recently the concept of a synthetic instrument was defined as a virtual instrument that is purely software and performs specific synthesis, analysis or measurement function on completely generic measurement agnostic hardware. Modern Scanning Probe Microscopes (SPMs) based on virtual instrumentation concepts are designed primary to obtain high resolution images and they may be used in material processing application with limited performance.

The ideal human interface for a Scanning Probe Microscopy (SPM) might present its user with a scaled-up 3D representation of the surface that can be probed and modified with a physical hand-held tool. The control system translates tool motion into a motion of the SPM tip and translates measured surface parameters into a pushing back force on the tool, as well as visual representations of surface data. When using such a system, the scientist is interacting directly with the surface itself. Natural motions of head and hands are used to investigate and sculpt the nanosurface like this is physically present at the scale of the scientist. This system allows the scientist to concentrate fully on investigating the surface and its features, rather than on programming the Graphical User Interface (GUI).

The nanomanipulator is obtained by integration of a scanning probe microscope (NTegra Vita) with its controller, a SPIDAR (SPace Interface Devices for Artificial Reality) force-feedback device with its controller and PC computers with high graphics facilities. A 3D image processing introduces the augmented reality concept using a mix of images in a head-mounted display. The augmented reality environment provides enhanced media for scientist to view the real time SPM image and to feel the force feedback during nanomanipulation. This concept is expected to have wide applications; for example, during nanomanipulation in complex situations, computer graphics may combine surface rendering with hidden features. The significance of the virtual reality interface to the SPM is to simulate the presence of the scientist on the sample surface – telepresence.

There are presented two main areas of results obtained with our haptic interface (SPIDAR): a) using topography information like haptic signal to generate virtual sticky surface sensation and b) normal cantilever deflection to ensure full interaction between the scientist and the sample.

Inulins as new nanostructured materials for the design of enantioselective sensors

Raluca-Ioana van Staden¹(iustinvanstaden@yahoo.com), Simona-Cornelia Balasoiu¹, Grzegorz Bazylak²,
Jacobus Frederick van Staden¹, Hassan Y. Aboul-Enein³

¹*Laboratory of Electrochemistry and PATLAB Bucharest, National Institute of Research for Electrochemistry and Condensed Matter, Splaiul Independentei Str., 202, Bucharest, Romania,*

²*Department of Pharmaco-Bromatology & Molecular Nutrition, Faculty of Pharmacy, Collegium Medicum, Nicolaus Copernicus University, Jagiellonska 13, PL-85-067 Bydgoszcz, Poland*

³*Pharmaceutical and Medicinal Chemistry Department, The Pharmaceutical and Drug Industries Research Division, National Research Centre, Dokki, Cairo 12311, Egypt*

Rezumat

Inulins are proposed as new electroactive materials in the design of enantioselective sensors, for the enantioanalysis of chiral drugs. Three types of sensors based on inulins were designed: enantioselective, potentiometric membrane electrodes; amperometric electrodes; and due to the nanostructured characteristic of inulins, it was possible to design stochastic sensors. The advantage of using stochastic sensors for such measurements is the possibility of qualitative and quantitative assay of the enantiomers in one analysis. The matrices used for the design of the sensors were carbon and diamond paste. Captopril was used as model analyte for proving the enantioselectivity of the proposed electrodes. While the potentiometric electrodes were used on linear concentration ranges up to 10^{-6} mol/L captopril magnitude order, the amperometric and stochastic electrodes were used up to 10^{-12} mol/L captopril magnitude order. The recovery of captopril enantiomers was higher than 90.00%, when it was performed either in synthetic samples (containing different ratios of enantiomers) or in real samples. The main advantages of using such sensors in enantioanalysis are: minimal processing of sample (usually its dissolution in water), high reliability of the analytical information, low limit of detection, and low cost of analysis.

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Nanostructures based on metallic nanoparticles and biomolecules

Stela Pruneanu*, Florina Pogacean, Liliana Olenic, (* stela.pruneanu@itim-cj.ro)

National Institute of R&D for Isotopic and Molecular Technologies, Cluj-Napoca, Romania

We described the preparation of a nanostructured assembly (amino acid layers/AuNPs) on the surface of a glassy carbon electrode (GCE). The surface was initially covered by a thin poly(glutamic) acid film, followed by covalent linking with L-cysteine molecules. The thiol groups from L-cysteine molecules were used to immobilize gold nanoparticles (mean diameter ≈ 40 nm). The results show that the amino acid layers/AuNPs can be used for the construction of composite materials with excellent electrocatalytic properties regarding the atenolol oxidation. The design chosen for the construction of this assembly was based on a delicate balance between the organic linker molecules, which are less conducting, and AuNPs, which ensure the electrical conduction path to the GCE surface. This nanostructured assembly allowed the detection of atenolol in low concentrations (down to 3.9×10^{-7} M). A similar approach (combination of amino-acids and metallic nanoparticles) can be further developed for the accurate and specific detection of various bio-chemical molecules. Morphological and electrochemical characteristics of the nanostructured layer were investigated by Atomic Force Microscopy (AFM), Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS).

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Nanoparticule multifunctionale pe baza de siliciu pentru tratamentul cancerului

Adina Bragaru¹, Irina Kleps¹, Mihaela Miu¹, Monica Simion¹,

Florea Craciunoiu¹, Sabin Cincea², Mirela Diaconu³

¹- INCD pentru Microtehnologie Bucuresti, ²- Institut Oncologic Bucuresti,

³- INCD pentru Stiinte Biologice Bucuresti

Tratamentul clasic al cancerului presupune excizia tesuturilor tumorale combinata cu chemoterapie, imunoterapie sau tratament cu radiatii, dar in functie de locatia si de raspandirea tumorii in tesuturile vecine, operatia nu este intotdeauna posibila. Prin urmare, dezvoltarea de noi tehnici care sa elibereze selectiv substanta activa si care sa nu altereze tesuturile sanatoase vecine a devenit una dintre cele mai atractive arii de cercetare in domeniul cancerului.

Odata evidentierea proprietatilor de biocompatibilitate si biodegradabilitate ale siliciului poros (PS) [1], s-au intensificat studiile pentru utilizarea acestui material in domeniul biomedical. Structura obtinuta prin corodarea electrochimica, de tip fagure, prezinta o arie a suprafetei foarte mare, ceea ce face sa fie o matrice ideala pentru inglobarea, in stare legata sau libera, a unei cantitati mari de medicament si care sa permita un control eficient al eliberarii acestora.

In lucrarea de fata s-a urmarit dezvoltarea unui sistem nanostructurat pe baza de siliciu pentru vectorizarea si cedarea monitorizata a substantelor active biologic, de interes terapeutic. Obtinerea particulelor cu dimensiuni submicronice, nanostructurate in volum, s-a realizat prin utilizarea unui proces de porozificare selectiva, prin alternarea densitatii de curent aplicate, care a condus la o structura multistrat, interfata dintre ele constituindu-se in plan de clivare [2]. Odata realizate microparticulele de Si, functiile dorite au fost atinse prin impregnarea cu nanoparticule superparamagnetice de oxizi de fier si de medicamente (dacarbazina si bleomicina), care au fost integrate intr-o matrice organica, polimerica (chitosan, dextran), pentru a facilita procesul de administrare catre zonele de interes din organismul uman sau animal.

In afara analizelor fizico-chimice de verificare a proceselor de functionalizare a particulelor au fost utilizate metode de evidentiere a reactiilor de toleranta sau respingere de catre organismul animal precum si de morfometrie computerizata pentru a se verifica biocompatibilitatea si functionalitatea sistemul propus.

Studiile in vivo au fost realizate pe sobolani Wistar, atat pe animele sãnãtoase, cat si pe animale cu tumori experimentale induse – hepatom RS1, realizandu-se douã suspensii, de concentratii 16 mg/ml, si 8 mg/ml, urmarindu-se ca parametri, toleranța locală, generala si rata de supraviețuire si mortalitate dar si sporul în greutate, aspectul tumoral- volum, greutate si aspect macroscopic, rezultatele obținute fiind favorabile, dependente de doză.

Se poate deci aprecia că nanoparticulele de siliciu pot acționa ca vectori de transport ai unor produși antitumorali, rezultat ce sugerează necesitatea studiilor si pentru testarea altor compusi medicamentosi legati de nanoparticule, precum și a altor forme de tumori experimentale.

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Lucrare invitata

Oxides nanotubes and their applications

Maria Zaharescu, mzaharescu@icf.ro

Ilie Murgulescu Institute of Physical Chemistry of the Romanian Academy, Bucharest

The discovery of the carbon nanotubes in 1991, has opened the interest for the preparation of inorganic nanotubes. Among the numerous inorganic compounds prepared as nanotubes the layered d-metal dichalcogenides MX_2 ($M = Mo, W, Ta$; $X = S, Se$), other type of chalcogenides as: $InS, ZnS, Bi_2S_3, TiS_2, TiSe_2, CdS, CdSe, Ag_2S$, boron nitride (BN), carbide (BC_x) and carbonitride ($B_xC_yN_z$), semiconducting materials, such as: $SiGe, InGe/GaAs, InGaAs/GaAs, SiGe/Si$ and $InGeAs/GaAs$, nanotubes of metals: Co, Sb, Se, Bi but also p-, d-, f-metal ($Al, Si, Ge, Ti, Nb, Ta, Zr, V, Mo, Dy, Tb$) oxides could be mentioned. The presentation will be focused on the oxide nanotubes preparation and their structural and morphological characterization. TiO_2, SiO_2, ZnO nanotubes, obtained by hydrothermal and by chemical methods in the presence of templating agents, present different size, structure and morphology [1,2], that makes them suitable for several application as, catalysis [3], as biological active materials [3] or gas sensors. Results obtained in testing the synthesized nanotubes in such application will be also discussed.

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Electromagnetic field propagation in graphene in the range 40 MHz-110 GHz

Mircea Dragoman^{1*}, George Konstantinidis², George Deligeorgis^{2,5}, Dan Neculoiu³, A.A.Muller¹
Daniela Dragoman⁴, Alina Cismaru¹, Robert Plana⁵

¹ National Institute for Research and Development in Microtechnology (IMT), Bucharest, Romania

² Foundation for Research & Technology Hellas (FORTH), Crete, Hellas

³ Politehnica University of Bucharest, Electronics Dept., Bucharest, Romania

⁴ Univ. Bucharest, Physics Dept., Bucharest, Romania; ⁵ LAAS CNRS, Toulouse, France

Similar to the famous Moore law, the Edholm law states that the need for higher bandwidths in wireless communications will double every 18 months. Today, for the wireless LANs, the carrier frequencies are around 5 GHz and the data rates are 110-200 Mb/s. However, according to Edholm law, wireless data rates around 1-5 Gb/s are required in few years from now [1]. This means that the carrier frequencies for wireless communications should become higher than 60 GHz. However, in this bandwidth the devices and circuits able to form a wireless link at room temperature are very scarce.

This limitation is due to relative high charge scattering rate and relative low mobilities encountered in all semiconductors at room temperature. Graphene is seen as a serious candidate able to solve this bottleneck since it displays a large mobility and a quite large mean-free paths of the carriers (3-400 nm) at room temperature much greater than the existing resolution of electron nanolithography and other nanotechnologies which is around 20 nm or less [2]. Since graphene is compatible with standard clean-room technologies, the ballistic transport at room temperature in graphene is seen as a way of ultrafast nanoelectronic devices able to work beyond 100 GHz. However, the data about graphene behavior at such high frequencies is very poor. So, the role of our communication is to fill this gap. We have fabricated a coplanar waveguide on graphene, we have measured its transmission and reflection parameters and so we were able to find an equivalent circuit on the entire bandwidth encompassing RF, microwaves, millimeter waves, and sub-THz domain. Moderate attenuations are found around 9 dB, the impedance of graphene is tunable via an applied dc voltage in the range 40-75 Ω , so graphene is very suitable for ultrafast devices in contrast to any other nanomaterial which cannot be matched at an impedance to 50 Ω . The way for THz applications of graphene is now open!

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Progresses in manufacturing of acoustic devices for GHz applications based on GaN/Si using micromachining and nano-lithographic technologies

A. Muller¹, D. Neculoiu¹, A. Dinescu¹, A. Stefanescu, A. Cismaru¹, I. Petrini¹, C. Buiculescu¹
G. Konstantinidis², T. Kostopoulos², A. Stavrinidis²

¹IMT Bucharest, Bucharest, Romania; ²FORTH-IESL-MRG Heraklion, Crete, Greece

Surface acoustic wave (SAW) and film bulk acoustic resonators (FBAR) have attracted a major interest in the fabrication of radio frequency (RF) filters for mobile and satellite communication systems, navigation, various forms of data transmission (WLAN). Most SAW resonators used in the actual mobile communication systems are manufactured on quartz, lithium tantalite or lithium niobate.

High impact of SAW and FBAR resonators, working in the GHz frequency range, is expected in the near future in communication and sensing applications (the sensitivity of these devices is proportional with the square of the resonance frequency). In both cases monolithic integration with other circuit elements could be beneficial. The use of GaN based acoustic devices has as major advantage the easily monolithic integration of the devices with other circuit elements (like HEMT transistors) on the same substrate.

Recent progress of GaN technology and especially the increasing of the quality of MOCVD grown layers on silicon offers the possibility to use these material in acoustic resonator manufacturing. GaN/Si is easily to be processed, using typical semiconductor-type technologies. On GaN grown on a silicon substrate it is also easily to develop micromachining technologies necessary in FBAR manufacturing and sub-micronic lithographic processes useful in GHz SAW resonator development. The paper will describe the progress in development of FBAR resonators on GaN/Si as well as, the progress in fabrication of SAW devices of different geometries with fingers and interdigits up to 100 nm wide. Resonance frequencies close to the X band have been obtained. The results represent the actual state of art in this topic.

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Microparticles synthesized by high pressure spraying method and their adsorption properties for phenol derivatives

Sandu Peretz¹, Dan F. Anghel¹, Manuela Florea-Spiroiu², Daniela Bala²,
Cristina Stoian³ and Gheorghe Zgherea³, peretz@icf.ro

¹ *Institute of Physical Chemistry "I. Murgulescu", Department of Colloids, Bucharest, Romania*

² *University of Bucharest, Department of Physical Chemistry, Bucharest, Romania*

³ *University "Dunărea de Jos" of Galați, Department of Chemistry, Galați, Romania*

Microparticles are synthesized by biopolymer chitosan (Chi) interaction at high pressure with sodium bis-(2-ethyl hexyl) sulfosuccinate (AOT) an anionic branched chained surfactant. The particles are formed instantaneously when the drops of cationic biopolymeric solutions come into contact with anionic surfactant solution [1-3]. In order to obtain microparticles an experimental apparatus equipped with a high pressure cell was used. The biopolymer solution in contact with high pressure CO₂ sprayed into surfactant solution bath, through a stainless steel capillary nozzle forming the chitosan-surfactant complex like microparticles. At pressures higher than 2 MPa, microparticles are formed while under this value wires are obtained. The effect of experimental parameters including the spraying pressure and the distance between the nozzle and the surface of surfactant solution on size and shape of ultrafine particles was studied. A maturation step of 12-14 hours is required before separation by centrifugation of the obtained particles from the liquid phase containing the surfactant. They are washed 4 to 5 times with 100 mL ultrapure water on a microporous filter, then with ethanol to remove traces of surfactant, and finally freeze dried using an ALPHA 1-2 LD plus apparatus. The chitosan-surfactant complex formation is proved by Fourier Transform Infrared (FTIR) Spectroscopy, whereas scanning electron microscopy (SEM) is used to characterize the morphology, size and shape of the particles. The FTIR spectrum indicates the interaction between sulfonate groups of AOT with amino ones of chitosan. The microparticles are quasi-spherical in wet conditions and irregular after freeze drying and presenting a rough surface with many pores. Lyophilized microparticles were used to remove phenol and o-cresol from water, and the adsorption process showed a maximum efficiency in range of pH=7-8. The uptake of phenol and o-cresol increases with the amount of used particles and decreases with increasing of initial pollutant concentration. The adsorption occurs rapidly in the first 60-120 minutes followed by a slow process that takes about 520-600 minutes.

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Lucrare invitata

Soft magnetic nanocrystalline/nanostructured materials produced by mechanical alloying routes

Ionel Chicinaș¹, Viorel Pop², ionel.chicinas@stm.utcluj.ro

¹ *Materials Sciences and Technology Dept., Technical University of Cluj-Napoca, Cluj-Napoca, Romania,*

² *Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania*

Our presentation is an overview on the soft magnetic nanocrystalline/nanostructured powders/compacts obtained by mechanical alloying routes, centred on: (i) soft magnetic nanocrystalline powders produced by mechanical alloying, (ii) soft magnetic nanocomposite powders like MeFe₂O₄/(Fe-Ni, Ni-Fe-X) produced by mechanical milling, (iii) soft magnetic nanocrystalline composite materials produced from nanocrystalline mechanically alloyed powders and dielectric and (iv) soft magnetic nanocrystalline compacts produced by Spark Plasma Sintering from mechanically alloyed powders. Soft magnetic nanocrystalline powders from Ni-Fe (Ni₃Fe) and Ni-Fe-X-Y systems (Supermalloy, Hipernick, Rhometal, Mumetal) have been produced by mechanical alloying. Their structural and magnetic properties were studied by XRD, SEM+EDX, DSC+TG, Mossbauer and magnetic measurements. The MeFe₂O₄/(Fe, Ni, Fe-Ni-X) nanocomposite powders in which the ferrite and metal/magnetic alloy nanoparticles should be coupled by the exchange interaction can combine the high permeability and induction of the magnetic alloy with the high resistivity of the ferrite. The nanocrystalline soft magnetic composite materials produced from nanocrystalline powders and dielectric can have a higher permeability than classical soft composite magnetic materials and smaller core losses than nanocrystalline massive materials. The results presented are based on the research obtained in the PN II Programme in cooperation with ICPE Bucharest, INCDFTM Bucharest, INCDFT Iasi, Institute Neel, Grenoble and University of Rouen and in PCE IDEI Grant.

Strain engineering; a new trend in nanotechnologies

Doina Raducanu¹ (doina.raducanu@mdef.pub.ro), Vasile-Danut Cojocaru^{1,2}, Ion Cinca¹

¹Universitatea "POLITEHNICA" din Bucuresti

²INCD pentru Microtehnologie - IMT Bucuresti,

New tools in the nanotechnology domain are capable now to find solutions, manipulate and build materials at the nanometer scale; one of them is the so called strain engineering. Ultra-strength phenomena, subsidiaries to strain engineering, are not connected only with the classical concerns of mechanics of materials but also with the functional properties of materials. Strain engineering is a possibility of tuning of materials physical and chemical properties by stress; by controlling the elastic strain field one achieves desired electronic, magnetic, optical, phononic, catalytic, etc. properties in the component. This article presents an overview of the principal deformation phenomena and transformations associated of strain engineered nanomaterials and also some practical results as concerning ultra strength nanostructured Ti based alloys.

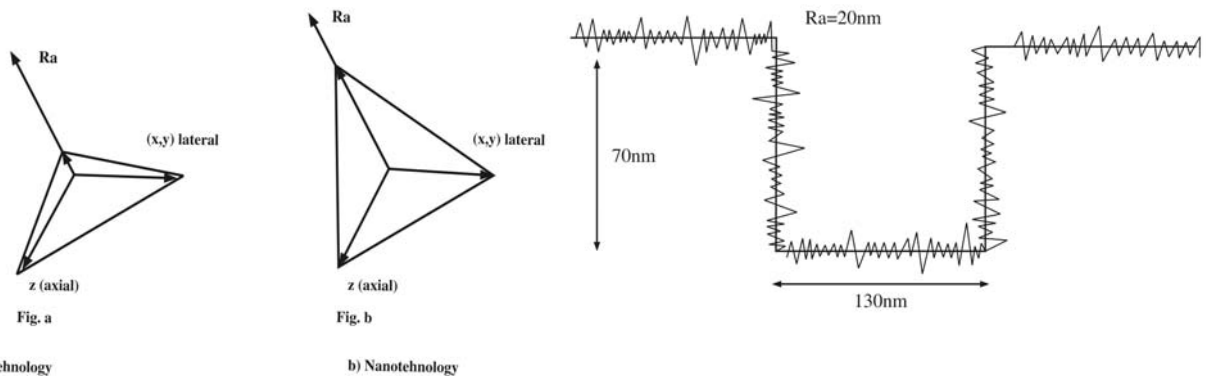
Roughness in nanotechnology: a new paradigm

D. Aostol, M. Bojan (mihaela.bojan@inflpr.ro), F. Garoi, I. Iordache

National Institute for Laser Plasma and Radition Physics

Dimensional nanometrology is the science and practice of measuring the geometrical characteristics of objects: dimension, shape, roughness, separation or displacement (in the 1-100 nm range). Metrology today, as in other hystorical periods of industrial revolution, assures the uniformity of measurements and mass production. This is the case of nanotechnologies these days. In order to go to mass production reproducible measurements are essential and without it the manufacturing of nanomaterials and nanostructures or MEMS and MOEMS is unconcievable.

Roughness can be measured with angstrom sensitivity for many years. (See Tolansky S., Microstructure of surface using interferometry, Ed. Eduard Arnold, London, 1968). Connected to nanometrology the roughness paradigm must be changed. Referring to Fig 1., the three axes define the geometry of a macroscopic system (e.g. lateral dimensions or 2D, axial or normal to the z direction, and finally the roughness dimension Ra).



For the macroscopic systems lateral and axial dimensions are very large as compared to roughness (Fig.1a). At nano scale objects the roughness is comparable with the other geometrical dimensions (Fig.1b). To understand this statement and the necessity of a new paradigm see Fig 2.

Two observations regarding some strange behaviours called our attention and started our interest, namely:

1. The stylus (contact) instruments are the most popular between scientists!
2. A force measuring instrument (e.g. Atomic Force Microscope) is used to investigate the roughness (geometry) at nanometric scale!

This paper experimentally addresses the questions we need to answer in order for a new paradigm to be imposed, as well as, it reviews the means, techniques, measuring technologies and characteristics of the novel instruments that are needed.

Nanotexturarea periodica a suprafetelor metalice cu pulsuri laser ultracurte

Catalina Radu¹, Adrian Dinescu², Marian Zamfirescu^{1,2*}

* marian.zamfirescu@inflpr.ro

¹Institutul National pentru Fizica Laserilor, Plasmei si Radiatiilor - INFLPR, Atomistilor Magurele, Ilfov, Romania

²Institutul National pentru Micro Tehnologii – IMT, Bucuresti, Romania

Prezentam o metoda de nanostructurare a suprafetelor metalice cu pulsuri laser ultracurte. La iradierea materialelor cu fluente laser la limita pragului de ablatie apar pe suprafata acestora structuri periodice induse de radiatia optica polarizata liniar. Perioada structurilor este mult sub lungimea de unda 775 nm a laserului Ti:Safir folosit. In cazul pulsurilor laser in domeniul femtosecundelor, perioada acestora variaza de la cateva zeci pana la sute de nanometri, in functie de conditiile de iradiere si de natura de materialului. Filme metalice din nichel, crom, platina, titan, depuse pe substrat de siliciu si sticla, au fost procesate prin scanare cu fascicul laser pulsant la diferite energii pe puls si viteze de scanare. La diferite conditii de iradiere s-au observat formarea a trei tipuri de structuri periodice: tipul I – structuri cu perioada de ordinul a 500-700 nm orientate perpendicular pe directia de polarizare a laserului; tipul II – structuri cu perioada la jumatatea celor de tipul I; si tipul III – structuri cu perioada sub 100 nm orientate paralel cu directia de polarizare a laserului. In cazul cromului s-a observat un al patrulea tip de nanostructuri, similar celor de tipul II, in sa cu perioada de aproximativ de patru ori mai mica decat a celor de tip I. S-a constatat ca orientarea structurilor nu depinde de directia de scanare cu laserul a suprafetei, ci urmareste doar directia de polarizare a laserului. Din caracterizari SEM s-a determinat formarea unor fire metalice cu lungimi de ordinul micrometrilor si grosimi de zeci-sute de nm. Masurari SEM "cross-section" au pus in evidenta adancimii ale structurilor periodice de pana la 200-300 nm, comparabile cu grosimea filmelor metalice. S-a mai determinat ca formarea acestora are loc in urma topirii si resolidificarii materialului si nu in urma ablatiei localizate, asa cum sugereaza teoriile interferentiale existente.

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Studii teoretice si experimentale de jonctiuni in Y pe baza de cristale fotonice

Mihai Kusko, Raluca Muller, Adrian Dinescu, Andrei Avram, Cristian Kusko (mihai.kusko@imt.ro)

Institutul National de Cercetare-Dezvoltare pentru Microtehnologie, Bucuresti, Romania

Lucrarea prezinta rezultatele simularilor si a experimentelor de fabricatie preliminara a divizoarelor de putere de tip jonctiuni in Y in cristale fotonice. Cristalele fotonice au proprietatea de a bloca transmitia radiatiei pentru anumite domenii de lungimi de unda, fapt care permite obtinerea de circuite de tip jonctiuni in Y cu unghi larg in cristale fotonice [1-3]. Pentru imbunatatirea performantelor este nevoie de utilizarea unui material cu indice mare de refractie precum nitru de siliciu. Au fost analizate structuri de cristal fonic de tip hexagonal cu atomi circulari obtinuti prin corodarea stratului de nitru de siliciu si cu ghiduri de unda obtinute prin indepartarea atomilor pe anumite portiuni. A fost simulata propagarea radiatiei cu lungimea de unda de 635 nm printr-un divizor de radiatie cu o intrare si doua iesiri care consta in jonctiunea in Y propriu-zisa si doua deviatii. Pentru scaderea nivelului de pierderi s-a luat in considerare racorduri la 30 de grade dintre ghidul de intrare si cele doua brate ale jonctiunii precum si intre bratele jonctiunii si ghidurile de iesire.

Simularea modului de propagare al radiatiei prin divizorul de radiatie a fost realizata cu ajutorul pachetului de simulare OptiFDTD. A fost utilizata o simulare tip 2D ca urmare a utilizarii metodei indicelui efectiv. Din rezultatele simularii s-a obtinut un divizor de putere care are o eficienta apropiata de cea ideala.

Din punct de vedere experimental s-a fabricat un cristal fonic cu o jonctiune in Y prin scrierea cu fascicul de electroni a unui strat de PMMA. In continuare prin structura imprimata in PMMA s-a realizat corodarea in plasma tip RIE a stratului de nitru de siliciu prin masca de PMMA. Structura obtinuta experimental probeaza fezabilitatea realizarii de circuite optice pe baza de cristale fotonice, utilizand litografia cu fascicul de electroni.

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Recent advancements in the development of a sensitive analytical platform based on magneto-optic surface plasmon resonance

Mihaela Gheorghiu, Sorin David, Cristina Polonschii, Dumitru Bratu, Eugen Gheorghiu
International Centre of Biodynamics, Bucharest, mgheorghiu@biodyn.ro

Recent developments within the International Centre of Biodynamics concerning chip preparation as well as accomplishment of a measuring set-up allowing magneto-optic surface-plasmon-resonance (MOSPR^{1,2}) assays are presented. The platform comprises the magneto-plasmonic sensor, the surface plasmon resonance detection module, the electromagnet providing the oscillating magnetic field (with controlled field strength and frequency) with actuation role for MOSPR and the flow-through chamber with integrated microfluidics.

The physical transduction principle is based on the combination of the magneto-optic activity of magnetic materials and plasmonic properties of selected metallic layers. The actual structure of layers was optimized using a Transfer Matrix approach 3-5 based on the magneto-optical activity of the trilayers as a function of the thickness and position of the Cr, Co and Au layers, and has been constructed in house via physical vapor deposition of thin layers of Cr, Au and Co.

Such combination can produce a significant enhancement of the SPR effects that strongly depends on the optical properties of the surrounding medium, allowing its use for biosensing applications². Calibration curves based on solutions with different refractive indices show a steeper slope in the case of the magneto-optical sensor proving an increased sensitivity. The sensing avenues emphasizing analytical capabilities of the platform e.g. to assess biomolecular reactions will be highlighted.

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Metode moderne de analiza nedestructiva cu radiatii X: Conditii , Limite, Perspective Aplicatii in studiul materialelor nanostructurate si Metrologia Nanotehnologiilor Aplicate

Mihai Danila, Mihaela Miu, Monica Simion, Adina Bragaru, (mihai.danila@imt.ro)
IMT Bucuresti

Lucrarea prezinta principalele metode de analiza nedestructiva cu radiatii X disponibile in IMT pe difractometrul cu anod rotitor Rigaku SmartLab Thin Film Diffraction System, principalele conditii experimentale, limitele si perspectivele acestora.

Acestea sunt subliniate prin prezentarea unor rezultate experimentale obtinute in IMT in metrologia cu radiatii X a materialelor nanostructurate policristaline & monocristaline (structura&compozitie de faze cantitativa/calitativa, metrologia grosimilor filmelor subtiri, metrologia straturilor epitaxiale: compozitie, deformare, mismatch, etc). Sunt prezentate unele rezultate obtinute in metrologia nanotehnologiilor de productie a nanomaterialelor carbonice (grafene, oxizi de grafena), ZnO, etc.

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3. "Biodegradation of Poly(vinyl alcohol) and Bacterial Cellulose Composites by *Aspergillus niger*", Anicuta Stoica-Guzun, Luiza Jecu , Amalia Gheorghe, Iuliana Raut ,Marta Stroescu, Marius Ghiurea, Mihai Danila, Iuliana Jipa, Victor Fruth, *J Polym Environ*, DOI 10.1007/s10924-010-0257-1, Online ISSN pg 1566-2543, 2010, Study supported by the project PNCDI II 32-115, with financial support from the European Social Fund, POSDRU/89/1.5/S/54785 project: "Postdoctoral Program for Advanced Research in the field of nanomaterials"

Nanostructured films of anodized TiO₂ in a fluorine electrolyte for solar cells applications

E. Manea, C.Obreja, M. Purica ,V. Schiopu, F.Comanescu, E. Budianu
IMT- Bucharest

TiO₂ samples for solar cells applications were prepared by the electrochemical oxidation of pure titanium thin film deposited onto various substrate types including silicon, SiO₂ and borosilicate glass. Titanium layers of 90 nm thickness were deposited on substrate by DC magnetic sputtering.

The influence of anodizing parameters on the surface morphology was investigated in detail to optimize the process in order to obtain the porous structure. The best results have been obtained using fluorine-containing electrolyte. After anodization, samples were washed in distilled water, dried with nitrogen and treated at different temperature from 400 to 800 °C for oxidation.

Thickness dependence of TiO₂ layers and pores geometry on the parameters of anodizing process was established from the SEM . The formation process of the porous structure and the change in surface morphology induced by heat treatments is evident.

The surface chemical compositional analyses of TiO₂ anodization and annealing films were performed by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of samples were recorded at 45°, in the 4000-370 cm⁻¹ spectral range. The IR spectra of the sample of titanium metallic film deposited on silicon substrate, puts in evidence the native tendency of titanium to oxidize in air, demonstrated by the appearance a spectral bands in the region 700-500 cm⁻¹, bands can be attributed to Ti-O bonds. Spectral band centered at 439 cm⁻¹ is characteristic mode of vibration of Ti-O-Ti bonding of anatase – phase.

From the Raman spectra one can conclude that the titania undergo following structural transformation at each stage of annealing process. At sample treated at 500 °C, anatase phase becomes the major one proved by the bands at 144 cm⁻¹ and 639 cm⁻¹ of Eg Raman active mode in anatase crystal.

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Studiul apoptozei celulelor tumorale indusa de hipertermia magnetica

Marioara Avram¹, Vasilica Schiopu¹, Andrei Avram¹, Antonio Radoi¹, Alina Popescu¹, Marius Volmer²

marioara.avram@imt.ro

¹ INCD pentru Microtehnologie, ² Universitatea "transilvania" Brasov

Apoptoza este o forma de moarte celulara organizata si foarte strict controlata enzimatic. In timpul apoptozei, membrana plasmatica genereaza corpii apoptotici (CA). Pentru a facilita recunoasterea CA de catre fagocite, celula semnalizeaza mediului extracelular starea sa apoptotica prin modificarea moleculelor de fosfatidilserina si transportul acestora de pe fata citosolica a membranei pe cea extracelulara (Encyclopedia of Life Science, 2005). Apoptoza celulelor melanom B16 a fost studiata prin spectrometrie UV-viz si spectrometrie FTIR care permite identificarea legaturilor chimice superficiale ale probelor analizate: tesut sanatos, tumora proaspata si tumora tratata prin hipertermie magnetica (HM) cu nanoparticule γ -Fe₂O₃, in camp alternativ cu frecventa de 120 kHz si intensitate 45 Oe. Din punct de vedere al atribuirii benzilor spectrale se disting trei domenii importante pentru studiul de fata: 1) 3000-2800 cm⁻¹, zona caracterizata de benzi ce pot fi atribuite modului de vibratie al legaturilor de C-H existente atat in proteinele tisulare cat si in celulele lipidice din tumora proaspata; scaderea drastica a intensitatii benzilor spectrale in cazul tumorii tratata prin HM se poate explica si prin aparitia unui proces oxidativ la apoptoza celulara. 2) 1800-1350 cm⁻¹, zona caracterizata de benzi ce pot fi atribuite gruparilor amidice din scheletul proteic; pentru tumora tratata HM se observa o puternica deplasare a benzilor spectrale din aceasta regiune, concomitent cu aparitia unei benzi cu maxim centrat la 1724 cm⁻¹, ceea ce indica apoptoza celulara. 3) 1350-900 cm⁻¹, zona caracterizata de benzi ce pot fi atribuite legaturilor fosfodiesterice din acizii nucleici; aceasta este zona care ofera cea mai relevanta caracterizare a apoptozei celulare. Pentru tumora tratata prin HM banda 1080 -1030 cm⁻¹ se deplaseaza si creste foarte mult in intensitate (P=O), banda de la 1240 cm⁻¹ dispare total, concomitent cu aparitia unei noi benzi spectrale la 1283 cm⁻¹, ca urmare a unui proces oxidativ, caracteristic apoptozei celulare.

Nanovezicule elastice utilizate ca vectori de transport transdermic ai hormonilor steroidieni. Studii de preparare, caracterizare si evaluare in vitro.

Cristina Hlevca* (chlevca@yahoo.com), Cristina Dinu Parvu** (ecristinaparvu@yahoo.com), Luigi Silvestro *** (dreispharma@aol.com), Alina Ortan **** (alina_ortan@hotmail.com), Patrut Elena* (patrutel@yahoo.com)

*Institutul National de Cercetare - Dezvoltare Chimico Farmaceutica, ICCF Bucuresti

**Universitatea de Medicina și Farmacie "Carol Davila" din București

*** S.C. Pharma Serv International srl din Bucuresti

**** Universitatea de Stiinte Agricole si Medicina Veterinara din Bucuresti

Principala dificultate a realizarii unui sistem transdermic este permeabilitatea scazuta a pielii. Una din modalitatile de realizare a transportului transdermic al medicamentelor prin piele este utilizarea nanoveziculelor elastice. Lucrarea prezinta studiile experimentale de preparare si caracterizare a unor nanovezicule elastice, transferozomi si etozomi, cu drospirenona (1), un hormon cu proprietati asemanatoare progesteronului, utilizat in terapia de substitutie hormonala si pentru contraceptie, in vederea realizarii unui sistem transdermic. S-a urmarit si influenta parametrilor de formulare asupra caracteristicilor nanoveziculelor: gradul de incorporare, stabilitatea in timp si cinetica de cedare. S-au preparat transferozomi prin metoda clasica a hidratarii filmului lipidic (2). Etozomii au fost preparati prin metoda descrisa de Touitou (3). Determinarea gradului de incorporare s-a efectuat prin determinarea cantitatii de drospirenona din 0,2 ml suspensie lipozomala, prin spectrofotometrie in UV si HPLC dupa prealabila separare a substantei neincorporate, prin centrifugarea la 12000 rpm, timp de 60 minute. Distributia pe dimensiuni a nanoveziculelor s-a determinat cu aparatul Mastersizer 2000 R, Malvern. Studiile de cedare in vitro s-au efectuat intr-o celula Franz verticala, modificata, utilizand membrana de celofan standard.

Experimentarile efectuate au demonstrat ca gradul de incorporare al drospirenonei in lipozomi precum si viteza de cedare a drospirenonei prin membrane sunt puternic influentate de compozitia transferozomilor (raportul molar dintre fosfatidil colina, colat de sodiu si drospirenona) si etozomilor (procentul de alcool etilic, fosfatidil colina si drospirenona din formulare).

Pe baza studiilor efectuate s-au ales cateva formulari cu grad mare de incorporare (75-95%) si viteze mai mari de cedare (40-86% din drospirenona in 24 ore) in vederea efectuarii studiilor in vivo si a conditionarii pentru realizarea sistemului transdermic. Finantare: Program PNCDI II, Proiect LIPHORM, Sept.2007-Sept.2010.

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Photocatalytic degradation of Eosin Y dye using SnO₂ nanocomposites

Claudia-Mihaela Hristodor, Narcisa Vrinceanu, Violeta-Elena Copcia,
Daniel Gherca, Eveline Popovici (hristodorc@yahoo.com)
"Al. I. Cuza" University of Iasi, Faculty of Chemistry

The tin oxide based nanocomposites have been used as efficient and environmentally benign catalysts. The developed protocols using this kind of material are advantageous in terms of simple experimentation, reusable catalyst, excellent yields of the products, short reaction time and preclusion of toxic solvents. In this work, we have reported novel synthesis and characterization of supported SnO₂ catalysts. The photocatalytic degradation of Eosin Y dye, an anionic xanthene fluorescent dye, has been investigated in aqueous heterogeneous solutions containing SnO₂ as photocatalysts. Toxicity experiments showed a reduction of the toxicity of an eosin Y dye solution of photocatalytic treatment.

Suprafete textile functionalizate bioactiv tip bariera cu proprietati antialergice/antimicrobiene

Loti Cornelia OPROIU¹ (lotio144@yahoo.com), Anca Angela ATHANASIU¹, Elena IONITA¹, DEACONU Marian¹, RUSE Mircea¹, ALBULESCU Viorel Liviu¹, Sanda DONCEA¹, Simona POP¹, TOLESCU Ciprian¹, FARAON Victor Alexandru¹, Anca Maria TOIU², Marieta NICHIFOR³, RADU Cezar-Doru⁴, Mihaela HRITCU⁴, Lucia CHIRITA⁵, Elena Alina NANU⁵, Stela FLORESCU⁶

¹INCDCP ICECHIM-Bucuresti ; ²Universitatea de Medicina si Farmacie- Cluj-Napoca ³Institutul de Chimie Macromoleculara "Petru Poni"- Iasi ; ⁴Universitatea Tehnica "Gh. Asachi" - Iasi ; ⁵S. C. BIO HIGH TECH srl; ⁶S.C. CHEMIX srl

Lucrarea prezinta prezinta studii experimentale recente efectuate in cadrul dezvoltarii cercetarii in domeniul realizarii unor tesaturi/ suprafete textile cu proprietati antialergice/ antimicrobiene de tipul bariera dubla: bioactiva-fizica.

Alergenii si microorganismele sunt prezente in viata noastra de zi cu zi fara ca noi sa le remarcam prezenta. Ele vin in contact direct cu organismul prin ingerare, cu pielea umana, caile nazale sau prin intermediul textilelor.

Reducerea cauzelor/calmarea suferintelor, pruritului raspunsurilor alergice ale organismului prin utilizarea unor tesaturi/tricoturi cu proprietati antialergice/antimicrobiene pentru diferite articole de imbracaminte incluzand si ciorapii/sosetele, dar si alte articole precum cele ce tin de lenjerie de pat sau alte decoratiuni interioare (mai ales draperii, perdele, canapele/fotolii tapitate), va ajuta persoanele alergice/potential alergice, sa reduca cantitatea de medicamente prescrise intre care Cortizonul este cel mai dur, sa creasca calitatea vietii lor.

Cercetarile au fost continuate in vederea obtinerii suprafetelor textile antialergice/antimicrobiene dorite, prin utilizarea unor produse, metode/tehnici si nanocompozite, intr-un mod original.

- Au fost realizate tratamente cu trei extracte naturale cu un continut de compusi bioactivi cu actiune sinergica antialergica/antimicrobiana, prin: imobilizare/legare cu ajutorul unor materiale polimerice acrilice; imobilizare/legare de un silan, cu obtinerea unor filme compozite bioactive dupa uscare/legare chimica; incorporare/imobilizare/nanoencapsulare intr-o masa/matrice sol-gel, care dupa gelifiere si uscare sa duca la obtinerea unor filme compozite bioactive. Acestea din urma pot sa contina sau nu si un material polimeric acrilic care prin reticulare sa asigure o rezistenta mai buna a filmului la suprafata textila.

- Au fost realizate, de asemenea, studii experimentale de sinteza a unor solutii/suspensii de oligomeri/polimeri sintetici functionalizati de catre partenerul de la ICMPP-Iasi.

- Au fost realizate: caracterizari fizico-chimice specifice acoperirilor compozite polimerice; caracterizari dermatologice in vivo pe subiecti umani, specifice; determinarea penetrarii, actiunii si citotoxicitatii compusilor bioactivi prin studii in vivo pe sobolani si cobai; caracterizarea mecanismului de initiere, dezvoltare si eliberare de mediatori la un episod alergic precum si caracterizari fizico-mecanice, chimice si coloristice ale suprafetelor textile.

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Nanostructured mesoporous silica as carriers for some antihypertensive agents

Roxana Florentina POPOVICI¹, Iuliana Florentina ALEXA², Narcisa VRANCEANU², Maria IGNAT², Eveline POPOVICI² and VICTOR A.VOICU¹ eveline@uaic.ro; evelinepopovici@yahoo.com

¹ *University of Medicine and Pharmacy "Carol Davila", Department of Clinical Pharmacology and Toxicology, Bucharest, Romania*

² *Department of Materials Chemistry, Faculty of Chemistry, "Al. I. Cuza" University of Iasi, Romania*

Considerable research efforts have been directed in recent years towards the development of silica mesoporous carriers as controlled drug delivery matrices whose properties are controlled not only by the chemical composition also by their properties such as stable uniform porous structure, high surface area, tunable pore size and well-defined surface properties. Moreover, their biocompatibility, high in vivo stability, low toxicity, high carrier capacity, feasibility of incorporation in their structure of both hydrophilic and hydrophobic drugs, and feasibility of variable routes of administration have improved their applicability.

In this work, SBA-15 mesoporous silica was used as carrier for the following antihypertensive agents - Captopril (the first ACE inhibitor) and Aliskiren (the first in a direct rennin inhibitor) - in order to obtain controlled release formulation.

The main advantages of the obtained drug delivery systems are the gradual drug release behavior and the lack of toxicity, which open the opportunity for their prospective uses as for considering them as potential formulations with only once daily administration.

Descrierea atomistica a nanostructurilor

Titus Sandu (titus.sandu@imt.ro)

Institutul National de Cercetare si Dezvoltare in Microtehnologie, Bucuresti

Lucrarea prezinta aplicatii ale metodei atomistice denumita metoda Tight-Binding (TB) in literatura de specialitate. Metoda TB este folosita cu succes pentru calculul proprietatilor electronice si optice atat la nivel empiric cat si ab-initio. Calitatea principala a metodei TB este faptul ca mentine caracterul atomistic al fenomenului descris, calitate care este esentiala pentru descrierea sistemelor nano.

Datorita eficientei computationale, metoda TB empirica, care foloseste parametrii ajustabili in functie de experimente sau calcule mai exacte, este larg folosita pentru descrierea la nivel nanoscopic a structurilor si sistemelor complexe precum interfetele dintre solide, defectele din cristale, aliajele, materialele amorfe, nano-clusterii cat si dot-urile cuantice. Metodele TB empirice sunt pana la 3 ordine de marime mai rapide decat metodele ab-initio bazate pe metoda functionalei densitate (density functional theory-DFT).

Pe de alta parte, metoda TB ab-initio numita DFT-TB-LMTO (DFT-tight-binding-linear muffin-tin orbitals) nu are niciun parametru ajustabil si este utilizata nu numai pentru descrierea cristalelor dar si pentru sistemele de dimensionalitate redusa cum ar fi structurile in staturi de ordinul nanometrilor.

In aceasta lucrare voi aborda descrierea TB pentru o serie intreaga de sisteme si probleme cum ar fi: aliajele ternare formate din compusi binari cu constante de retea foarte diferite, precum si estimarea benzii interzise in sistemele mari, (posibil nano-clusterii) unde metodele DFT nu pot fi folosite cu succes [1]; folosirea metodei TB in calcule ale proprietatilor optice [2]; si transportul dependent de spin prin bariere de ordinul catorva nanometri atat la nivel empiric cat si ab-initio [3].

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Functionalizarea unor suprafete parte integranta a unui imunosenzor pentru cuantificarea proteinei de legare a acizilor grasi-fractia cardiaca (hFABP)

Dana Stan (dana_stan2005@yahoo.com)

Institutul National de Cercetare si Dezvoltare in Microtehnologie, Bucuresti

hFABP este un marker precoce al infarctului de miocard acut (IMA). Valorile plasmatiche cresc dupa 3h de la debutul IMA si revin la normal dupa 12-24h. Dinamica modificarilor concentratiilor plasmatiche ale hFABP este foarte asemanatoare cu a mioglobinei (Myo), numai ca hFABP prezinta o specificitate si sensibilitate superioara fata de Myo (1).

Recunoasterea specifica a anticorpului anti-hFABP pe suprafata, transformarea semnalului fizico-chimic produs de interactia cu proteina, intr-un semnal corespunzator (electric, optic), procesarea si amplificarea semnalului, constituie elementele principale pentru alcatuirea acestui imunosenzor.

Desi numarul si varietatea metodelor utilizate in alcatuirea imunosenzorilor este foarte mare, totusi specificitatea si selectivitatea sunt date de componenta biologica: alegerea potrivita a anticorpilor specifici si a parametrilor imunoreactiei (2).

Lucrarea prezinta: 1) functionalizarea chimica a doua suprafete solide: Au si SiO₂ cu formare de monostraturi autoasamblate, pentru imobilizarea covalenta a anticorpilor specifici; 2) imobilizarea covalenta a proteinei-test albumina bovina serica (BSA) 3) caracterizarea suprafetelor functionalizate prin metode fizico-chimice: FTIR-ATR, voltametrie ciclica, SEM; 4) stabilirea parametrilor reactiei Ac-Ag (anti-hFABP si hFABP) prin metoda ELISA, utilizand o suprafata nefunctionalizata de polistiren (3).

Formarea de filme organice subtiri pe suprafetele metalice utilizate le confera acestora proprietati superioare in construirea unor noi dispozitive de cuantificare a unor proteine de mare interes in diagnosticul IMA, cu inalta sensibilitate si specificitate si timp de raspuns rapid fata de metodele actuale.

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Analiza micromagnetica a unui sistem de tip Lab on a Chip

^{1,2}Marius Volmer (volmerm@unitbv.ro), ²Marioara Avram, ²Marius Andrei Avram

¹Universitatea "Transilvania" din Brasov, ²IMT Bucuresti

Lucrarea prezinta o analiza micromagnetica a unui sistem de manipulare si detectie a particulelor biologice marcate magnetic, ca parte a unui dispozitiv de tip Lab on a Chip (LOC). Se studiaza comportarea nanoparticulelor superparamagnetice in camp magnetic. Sunt considerate situatiile cand acestea sunt izolate sau in zona senzorului realizat din straturi magnetice subtiri. Pentru diametrul nanoparticulelor a fost aleasa o valoare de 200 nm si se considera permeabilitate magnetica relativa de aproximativ 28. Pentru magnetizarea de saturatie s-a considerat o valoare de 110 uem/cm³. Curbele de magnetizare simulate pentru nanoparticule sunt in bun acord cu rezultate experimentale (camp de saturatie, aspectul curbei, etc.) citate in literatura si pun in evidenta efectele de aglomerare si interactia magnetostatica dintre acestea si senzor. Pentru manipularea acestor nanoparticule se propune un model simplu de circuit electric, in forma de V. Se analizeaza profilul campului magnetic creat si sunt calculate fortele magnetice de interactie. Este evidentiat un efect de pozitionare cu precizie a nanoparticulelor. Efecte de autoaranjare a nanoparticulelor in zona senzorului magnetic au fost puse, de asemenea, in evidenta. Acest aspect se datoreaza unor campuri magnetice, cu gradienti mari, generate de catre senzori. Pentru detectia nanoparticulelor au fost considerati senzori spintronici cu efect magnetorezistent gigantica (GMR) si cu efect Hall planar (PHE). Prin simulari micromagnetice s-au obtinut caracteristicile de detectie ale acestor senzori in functie de numarul de nanoparticule magnetice. A fost pusa in evidenta o dependenta a caracteristicii de detectie de pozitia acestora in zona senzorului. In final sunt prezentate cateva rezultate experimentale preliminare obtinute de catre autori.

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Materiale compozite bazate pe nanotuburi de carbon si poli o-fenilendiamina

Mihaela Baibarac (barac@infim.ro), Ioan Baltog, Ion Smaranda, Malvina Scocioreanu,
Ilarie Gontia, Timucin Velula, Lucian Mihut
Institutul National de Cercetare Dezvoltare pentru Fizica Materialelor, din Magurele,
str. Atomistilor 105 bis, CP MG-7, Romania

Lucrarea raporteaza sinteza si proprietatile vibrationale ale materialului compozit bazat pe poli o-fenilen diamina si nanotuburi de carbon, utilizand ca agenti de propagare a lantului macromolecular compusi cu proprietati oxidante diferite precum acidul fosformolibdic ($H_3PMo_{12}O_{40} \times H_2O$) si $FeCl_3$. Utilizand spectroscopia Raman noi aratam ca interactia chimica a nanotuburilor de carbon cu un singur perete (SWNTs) cu $H_3PMo_{12}O_{40} \times H_2O$ conduce la nanotuburi de carbon functionalizate cu polioxometalati (SWNTs- PMo_{12}), structuri care pot fi folosite cu succes ca material activ de electrod pentru supercapacitorii electrochimici [1]. In acord cu studiile TEM, un rezultat al interactiei chimice a SWNTs cu $H_3PMo_{12}O_{40} \times H_2O$ este formarea unor fragmente de tub de lungime scurta, care se comporta din punct de vedere vibrational similar fullerenei. Un argument in acest sens este prezentat de noile linii Raman cu maximele situate la ca. 240-275 si 1450-1472 cm^{-1} asociate modurilor de vibratie Hg(1) si respectiv Ag(1). [2] Studiile corelate de imprastiere Raman exaltata prin plasmoni de suprafata si spectroscopie FTIR demonstreaza ca polimerizarea chimica a o-fenilen diaminei (OPD) in prezenta SWNTs- PMo_{12} conduce la formarea unor materiale hibride organic/anorganic de tipul poli o-fenilen diamina (POPD) dopata cu ioni de $[H_2PMo_{12}O_{40}]^- / SWNTs-PMo_{12}$. In cazul polimerizarii chimice a OPD in prezenta SWNTs si a $FeCl_3$ o functionalizarea covalenta a peretelui nanotuburilor de carbon este evidentiata in spectrele SERS, inregistrate la lungimea de excitare egala cu 514 nm, prin modificarea raportului intre intensitatile relative ale liniilor G^+ si G^- atribuite modului de vibratie tangential. Folosind spectroscopia FTIR, efecte de impiedicare sterica importante sunt evidentiata in cazul compozitului POPD/SWNTs- PMo_{12} . [3]

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Nanocompozit pe baza de argint pentru contactarea senzorilor de temperaturi inalte pe carbura de siliciu (SiC)

Florin Draghici¹ (f_draghici@yahoo.com), Gheorghe Brezeanu² (gheorghe.brezeanu@dce.pub.ro), Ion Rusu² (romcarfem@yahoo.com), Eugen Popa³ (dg@baneasac.ro),
¹Universitatea "Politehnica" Bucuresti, ²IMT Bucuresti, ³Baneasa S.A.

Dispozitivele electronice pe SiC ofera posibilitatea functionarii la temperaturi ridicate si in medii ostile. Unul din factorii limitativi in domeniul temperaturilor de lucru este contactarea dispozitivului. Desi acesta permite functionarea la temperaturi ridicate (maxim 800°C) pana in prezent dispozitivele incapsulate depasesc foarte rar 300°C. Tehnologiile utilizate in cazul Si nu au fost dezvoltate pentru temperaturi mai mari de 250°C, deoarece dispozitivele nu functionau peste 200°C. In cazul SiC este necesara conceperea unei tehnologii de contactare noi care sa nu limiteze functionarea dispozitivului in temperatura.

Prezenta lucrare propune o solutie pentru contactarea senzorilor de temperatura realizati pe SiC, respectiv, utilizarea unei paste nanocompozit pe baza de Ag care sinterizeaza la temperaturi joase desi punctul de topire este peste 900°C. Pasta a fost testata pentru o serie de aplicatii de putere (la vehicule electrice), sisteme optice (diode laser si LED de putere) si module de comunicatii. In lucrare se prezinta structura nanocompozitului, tehnica de sinterizare, modul de folosire. Folosirea acestei paste pentru senzorii de temperatura ofera garantia unor contacte robuste pana la temperaturi de 800 °C.

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The Influence on Polymer-Based Composites in the Morphology of Laser-Synthesized Carbon Nano-Fillers

Lavinia Gavrilă-Florescu^{1*} lavinia.gavrila@inflpr.ro, Ion Sandu¹, Ion Voicu¹

¹National Institute for Lasers, Plasma and Radiation Physics, P.O. Box MG-36, Bucharest, Romania
*IMT-Bucharest, 126A, Erou Iancu Nicolae street, 077190, PO-BOX 38-160, 023573, Bucharest, Romania

Keywords: laser-pyrolysis, carbon nanoparticles, graphene, composites

Carbon nanoparticles are considered high-potential filler materials for the improvement of mechanical and physical polymer properties. As the limited compatibility of this filler with most matrices constitutes an important bottleneck in the area of resulted nanocomposites, the focus of the work was to drive these materials into a regime where they can favorably interact with the matrix. Through variation of gas composition and experimental parameters, the laser-induced pyrolysis leads to carbon nanoparticles with different morphologies and, favored by the radical mechanism of formation and the presence of heterogeneous atoms, allows the in-situ functionalization with appropriate reactive groups. In connection with mechanic and electric properties of resulted composites, the powder characteristics were synthesized from C₂H₂/SF₆, C₂H₂/C₂H₄, C₂H₄/SF₆ and C₂H₂/C₂H₄/N₂O gaseous mixtures. For carbon nanopowders with an apparent density of 0.5 g/cm³ the measured values of their electrical resistivity were between 100 and 103 Ω.cm whereas for composites with a 5% wt. concentration of carbon nanoparticles in the polymer matrix the electrical conductivities ranged between 107 and 1015 Ω.cm. Some correlations between the nanoparticles' structure and polymer composites have shown that the aggregate mean dimension of the carbon nanoparticles could be more important in the electrical conduction of the composites.

Micro-structurare laser in materiale fotosensibile folosind absorbtia bifotonica.

Florin Jipa, Marian Zamfirescu, Andreea Matei, Razvan Dabu (florin.jipa@inflpr.ro)
INFLPR- Institutul National pentru Fizica Laserilor, Plasmei si Radiatiei

La iradierea materialelor cu pulsuri laser ultrascurte (femtosecunde), in centrul spotului laser focalizat, datorita fluentei laser extrem de ridicate, au loc procese de absorbtie multifotonica intr-un volum cu dimensiuni sub limita de difractie. In urma absorbtiei neliniare au loc modificari fizico-chimice ale materialului la nivel submicrometric.

In materialele de tip fotorezist folosite in fotolitografia clasica, transparente la radiatia NIR (infrarosu apropiat), putem focaliza pulsurile laser cu emisie la 800 nm in volumul materialului fara ca radiatia optica sa fie absorbita la suprafata. In procesul interactiei bifotonice, in centrul spotului laser focalizat unde intensitatea laser depaseste pragul efectului neliniar, materialul absoarbe doi fotoni la 800 nm, cu energie echivalenta cu a unui singur foton la 400 nm, initializand astfel procesul de fotopolimerizare a materialului. Deoarece procesul are loc doar in centrul spotului laser focalizat, prin fotopolimerizarea de doi fotoni pot rezulta structuri cu dimensiuni sub limita de difractie. Prin deplasarea controlata de calculator a fascicolului laser focalizat prin volumul materialului transparent se poate genera practic orice structura 2D si 3D dupa un design prestabilit.

In acesta lucrare prezentam metoda si instalatia de micro-structurare laser in materiale fotosensibile folosind absorbtia de doi fotoni, precum si structurile realizate. Folosind algoritmi similari metodei de tip rapid-prototiping s-au obtinut microstructuri 3D cu aplicatii in domenii precum microfluidica, suportii biologici pentru inginerie tisulara, dispozitive fotonice, tinte pentru experimente cu laseri de mare putere.

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Resonatoare circulare plasmonice

Cristian Kusko (cristian.kusko@imt.ro)
IMT – Bucuresti

Lucrarea prezinta functionalitatea unui rezonator circular plasmonic cu dimensiuni submicronice care opereaza ca add – drop filter [1] in infrarosul mediu. Se investigheaza numeric prin simulari de tip diferite finite in domeniul timp (FDTD) proprietatile modale si de cuplaj ale acestui tip de dispozitiv calculandu-se astfel caracteristica spectrala. Se considera influenta pierderilor radiatiei in metal si se optimizeaza parametrii geometrici pentru obtinerea unui factor de calitate ridicat.

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Proiectare de senzori refractometrici pe baza de cristale fotonice

Mihai Kusko, (mihai.kusko@imt.ro)
Institutul National de Cercetare-Dezvoltare pentru Microtehnologie, Bucuresti, Romania

In aceasta lucrare se prezinta rezultatele studiilor de proiectare a senzorilor refractometrici tip cristale fotonice din nitru de siliciu. Acest tip de senzori detecteaza variatia indicelui de refractie al mediului in care este imersat cristallul fonic ca urmare a interactiei radiatiei din cristallul fonic cu mediul inconjurator prin intermediul unei evanescente. Pe plan mondial au fost studiate mai multe configuratii de senzori pe baza de cristale fotonice planare cu o linie de defecte (ghiduri de unda) [1] sau cu microcavitati [2] Toate aceste tipuri de senzori functioneaza pe baza monitorizarii spectrului de transmisie prin cristallul fonic.

A fost simulata propagarea radiatiei prin cristale fotonice pe baza de nitru de siliciu pentru lungimi de unda din domeniul vizibil centrat in jurul valorii de 635 nm cat si cristale fotonice pentru domeniul infrarosu centrat in jurul valorii de 1550 nm. Parametrii cristalelor fotonice (constanta de retea, raza atomilor) difera functie de domeniul de radiatie utilizat. Simularea s-a realizat cu ajutorul metodei FDTD (finite difference time domain) utilizand pachetul de soft OptiFDTD. S-a observat o modificare a spectrului de transmisie al radiatiei prin cristale fotonice ca urmare a modificarii valorii indicelui de refractie al mediului inconjurator atat in cazul in care se considera radiatia din domeniul vizibil cat si in cazul in care se considera radiatia din domeniul infrarosu.

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The versatility of catalytic LCVD technique to grow carbon nanotubes

Iuliana Morjan (iuliana.soare@inflpr.ro)
INFLPR si INCD-Microtehnologie

The catalytic LCVD offers the advantage of high versatility and control since it separates the catalyst preparation from the catalytic growth of nanotubes. The method is characterized by the CO₂ laser thermal dissociation of volatile carbon-containing precursors over silicon substrates. Iron based core-shell nanocomposites (iron-based core surrounded by carbon) were employed as catalysts. Gas mixtures containing acetylene, sulfur hexafluoride and ammonia were used. Other main experimental parameters such as laser power and total gas pressure were also varied. It cannot be excluded that impurities like nitrogen may promote formation of coiled carbon nanotubes. Structural characterization of the samples by SEM, TEM, Raman spectroscopy and X-ray diffraction was performed.

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Silicon micro- and nano- structuring by etching with liquid chlorine and fluorine precursors using femtosecond laser pulses

Magdalena Ulmeanu (magda.ulmeanu@inflpr.ro)

*National Institute for Laser, Plasma and Radiation Physics, Laser Department,
Atomistilor Str. 409, P. O. Box MG-36, Magurele 077125, Romania*

The aim of this study is to investigate the micro and submicrometer scale structuring of the silicon by liquid chlorine and fluorine precursors with a 200 fs laser pulses at a wavelength of 775 nm and 387 nm. The silicon surface was irradiated at normal incidence, by immersing the Si substrates in a glass container filled with liquids, e.g. CCl_4 and $\text{C}_2\text{Cl}_3\text{F}_3$. We report that silicon surfaces develop array of spikes for single step irradiation at 775 nm, as well at 387 nm. When irradiating with 400 pulses, 330 mJ/cm^2 at 775 nm wavelength, the average height of the formed Si spikes for the case of fluorine precursors is $4.2 \mu\text{m}$, with a full width at half maximum of 890 nm. The chlorine precursors develops at the same wavelength irradiation, Si spikes with $4 \mu\text{m}$ height and $2.3 \mu\text{m}$ full width at half maximum, for irradiation with 700 pulses at 560 mJ/cm^2 fluence. Well ordered areas of submicrometer spikes with an average height of about 500 nm and about 300 nm wide have been created by irradiation at 387 nm by chlorine precursors, while the fluorine precursors fabricate spikes with an average height of 700 nm and about 500 nm wide. Atomic force microscopy and scanning electron microscopy of the surface show that the formation of the micro and submicro spikes involves a combination of capillary waves on the molten silicon surface and laser-induced etching of silicon, both at the 775 nm and 387 nm wavelength irradiation. The energy-dispersive x-rays measurements indicate the presence of chlorine and fluorine precursors on the structured surface. The fluorine precursors create more ordered area of Si spikes at both micro and submicro scale. The potential use of patterned Si substrates with gradient topography as model scaffolds for the systematic exploration of the role of 3D micro/nano morphology on cell adhesion and growth is envisaged.

Sectiunea B

Sectiunea C

Ultra thin – ultra strength Ti-based strips

Vasile-Danut Cojocaru^{1,2} (dan.cojocaru@mdef.pub.ro), Doina Raducanu², Ion Cinca²

¹*INCD pentru Microtehnologie - IMT Bucuresti,*

²*Universitatea "POLITEHNICA" din Bucuresti*

Titanium alloys are extensively used in a variety of applications due to their good mechanical properties and corrosion resistance. A Ti-25Ta-25Nb β -type titanium alloy was subjected to thermo-mechanical processing and testing with the aim to obtain ultra-thin strips with a thickness of about 36 μm . The obtained strips showed a nanocrystalline structure due to severe plastic deformation (SPD). Data concerning structural changes were obtained by X-ray diffraction, the results showed that in as-cast state the alloy consist in a mixture of β -Ti/ α -Ti/ NbTi_4 phases and in the case of SPD processed state, two β -Ti type sub-phases appear, both showing nano-size crystallites. Obtained mechanical properties were appropriate evaluated, the results showed that in the case of SPD alloy in comparison with as-cast state, a steep increase in ultimate tensile strength of about 255%, a high decrease in elongation to fracture of about 95% and a high increase in elastic modulus of about 130% were obtained.

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Innovative optical metrology technique for the characterization of periodic media

Petre Catalin Logofatu (plogofatu@yahoo.com)

Institutul National de Fizica Laserilor, Plasmei si Radiatiei, sectia Laser, Magurele, judetul Ilfov

The main concept of the project is the development of a innovative optical metrology technique for the characterization of periodic media. The determination of the grating parameters from optical measurements is called optical scatterometry [1-3].

We will also deal with the sensitivity of scatterometry, which is an element of increasing importance in the conditions of the miniaturization trend in semiconductor industry. Little literature is dedicated to the subject of increasing the sensitivity of scatterometry. The lack of research about the idea of using grating anomalies for increasing scatterometry sensitivity and the existence of an exotic, insufficiently studied type of anomaly which is able to provide us exactly the kind of sensitivity required are the main motivation behind the submission of this proposal.

The approach to the stated objective will consist in a multiple vector attack from multiple directions. One approach vector is, of course, the theoretical study of the anomaly, in the experimental conditions and for the type of grating we know that such anomalies do occur, the finding of its nature. Another approach vector is the creation of codes based on diffraction theories dedicated to periodic media. Scatterometry measurements will be done on gratings likely to show anomaly type-behavior. The scatterometer will have to be built and various components offering it various degrees of freedom will be added and integrated in its basic structure.

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Acoustic metamaterials: numerical analysis of negative refraction

Cristina Pachiu⁽¹⁾ (cristina.pachiu@imt.ro), Jean Louis Izbicki⁽²⁾

National Institute for R&D in Microtechnologies, Erou Iancu Nicolae 126A, Bucharest 077190, Romania E-mail: Laboratoire d'Acoustique Ultrasonore et d'Electronique LAUE UMR 6068 CNRS, Université du Havre, Place R. Schuman, 76610 Le Havre, France

Abstract: Metamaterials are artificial materials micro or nanoscale designed to elicit unusual and very useful properties at the macroscale.

The interest in acoustical metamaterials stems from scientific successes reported in the creation of electromagnetic materials, photonic crystals with band-gaps, negative refractive index and cloaking phenomena. Those results have inspired work in the acoustic domain on phononic crystals and metamaterials with special properties such as negative effective mass or negative stiffness for use as acoustical superlenses, cloaks and acoustic isolation.

A numerical analysis of negative refraction process is reported using a phononic crystal with an elastic solid matrix. The phononic crystal considered in this study is made of a periodic arrangement of holes in solid matrix. Dispersion curves are discussed and the conditions for which negative refraction can appear are identified.

Keywords: Acoustic metamaterials, Phononic crystal.

Analiza termică și caracterizarea microscopică a pulberilor de hidroxiapatită obținute prin precipitare umedă

Aurora Anca Poinescu (poinescua@yahoo.com)¹, Simona Pop (popsimfc@yahoo.com)²,
Rodica Mariana Ion (rodica_ion2000@yahoo.co.uk)^{1,2}
Universitatea "Valahia" din Targoviste¹ ICECHIM, Bucuresti²

În ultimele decenii, o serie de materiale de implant pe bază de hidroxiapatita ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), fosfați de calciu ($\beta\text{-Ca}_3(\text{PO}_4)_2$), și diverse compozite ceramice au fost utilizate în domenii ca ortopedie, neurochirurgie. Hidroxiapatita are aplicații și de acoperire a suprafețelor implanturilor metalice ortopedice și stomatologice. Pentru aceste aplicații hidroxiapatita are un dublu rol și anume, reduce eliberarea ionilor metalici acționând ca o barieră fizică, precum ajută și la pregătirea pentru înlocuirea de fragmente osoase. Pentru această lucrare au fost efectuate studii termice și microscopice asupra pulberilor de hidroxiapatita obținute prin precipitare umedă, la temperatura camerei. Analiza DSC a fost efectuată în aer cu o limită de temperaturi cuprinse între 25-550°C, cu o viteză de 200C/min într-un creuzet din aluminiu, analiza TGA s-a efectuat în atmosferă de N_2 , cu intervalul de temperatură cuprins între 25-1200°C și cu o viteză de 200C/min într-un creuzet din alumina (Al_2O_3) și analiza TGA în aer, intervalul de temperatură 25 – 1100°C, cu aceeași viteză. În imaginile SEM de hidroxiapatita, se pot vedea cristale mici (<100 nm), în particule aglomerate, cu o granulație cu o distribuție uniformă, și care corespunde unei cristalinități ridicată ale pulberi de hidroxiapatită, mai ales pentru pulberea obținută după calcinare la 10000C pentru 1h. Imaginile microscopiei electronice prin baleiaj au arătat cristalite crescute cu multe aglomerări sferice și puține cristalite de 0,1 μm . Metoda de sinteză prin precipitare umedă, a fost aleasă deoarece este calea cea mai reușită, datorită ușurinței în operațiunile experimentale, temperaturi scăzute de lucru, un procent ridicat de produse pure și un necesar de echipament ieftin.

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Structural and morphological properties of ZnO films obtained by Chemical Bath Deposition

V. Popescu^{1,2,#}, G. L. Popescu², M. Dănilă¹, A. Dinescu¹

#Corresponding author: violeta.popescu@chem.utcluj.ro

¹National Institute for Research and Development in Microtechnologies.

²Technical University of Cluj-Napoca, 400641 Cluj-Napoca, Romania.

Zinc oxide (ZnO) is a semiconductor that responds to ultraviolet (UV) light, having a wide band gap of 3.37 eV for bulk material, with various applications including light-emitting devices, solar cells, gas sensors being a promising material for short wavelength optoelectronic devices, especially for UV light-emitting diodes (LEDs) and laser diodes (LDs). ZnO films have been deposited onto commercial glass slides by Chemical Bath Deposition starting from solutions containing ZnSO_4 , NaOH and NH_4OH , at 80°C. The influences of the deposition time and solution concentration on the formation and the properties of the films were studied. X ray diffraction analysis revealed that the "as deposited" films consisted on well formed ZnO crystals (Fig 1). Thermal treatment (T) determined the increase of the crystallinity of the films. The deposition conditions influenced the growth directions, the density of the nanorods and the shapes of the crystals that formed the films (fig 2). Thermal treatments had a minor influence on the morphology of the films.

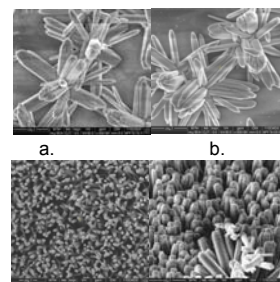


Fig. 2. SEM micrographs of ZnO films a. sample 5, b. sample 6 T, c. sample 7, d sample 8.

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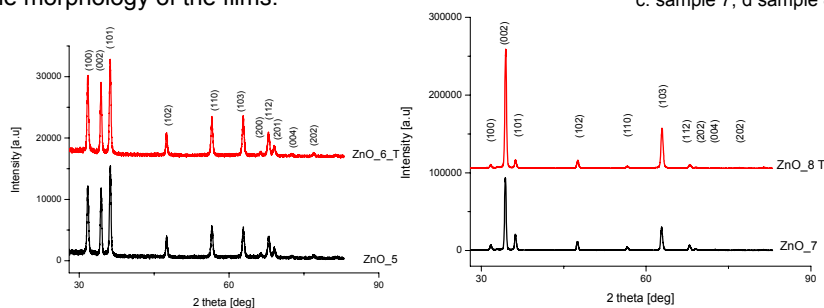


Fig.1. X ray diffraction patterns of as deposited and thermal treated (T) films

A new route for the hydrothermal synthesis of Eu doped tin oxide nanoparticles

D. Tarabasanu-Mihaila (doinat@infim.ro), L. Diamandescu, M. Feder, V.S. Teodorescu, A. Banuta
National Institute of Materials Physics, P.O. Box MG-7, Bucharest, 077125, Romania

In recent years, rare-earth doped tin oxide (SnO_2) has received much attention due to its chemical stability, high transparency in visible-light region and interesting fluorescence properties. As host material doped with Eu^{3+} it emits a unique reddish orange color. Several methods including sol-gel, hydrothermal, radio-frequency sputtering and the precipitation route have been applied to synthesize SnO_2 -based luminescent materials [1-3]. In all cases, at europium concentrations higher than 8 at%, a phase separation was observed. In this study, a new hydrothermal synthesis route of Eu^{3+} doped SnO_2 nanoparticles is reported. We succeed to increase the solubility range (up to ~ 12 at%) by a hydrothermal treatment at relative low temperature (250 °C), starting with metal chlorides as precursors. The as obtained and calcinated samples were characterized by X-ray diffraction (XRD), Mössbauer spectroscopy, transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and luminescence measurements. The nanocrystalline powders have the cassiterite structure (rutile type) and no phase separation was observed at Eu concentrations lower than 12 at %. As revealed by XRD and TEM measurements, the mean particle size is about 3-5 nm for as resulted samples and 5-10 nm for the calcinated powders.

Fig.1 shows the EDX spectrum of the hydrothermal sample with nominal atomic concentration of 6 at. % Eu. The determined atomic ratio Eu/Sn was found to be in the range 5.9/94.1 – 6.8/93.2, in good agreement with the nominal Eu/Sn concentration value.

The site occupancy of Eu^{3+} in nanoscaled SnO_2 lattice is also discussed.

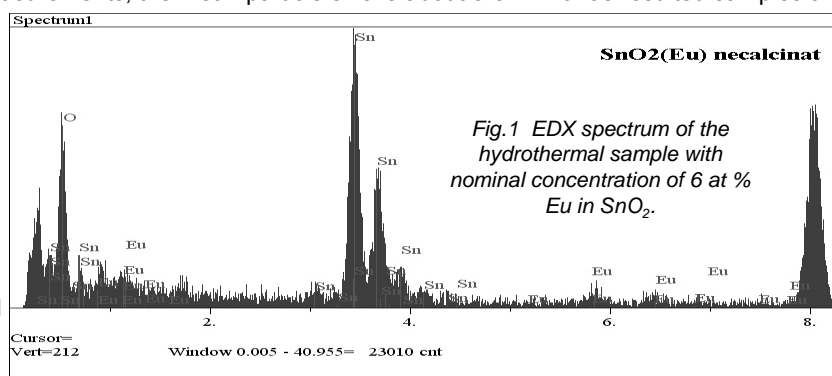


Fig.1 EDX spectrum of the hydrothermal sample with nominal concentration of 6 at % Eu in SnO_2 .

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Sulfonated polyetheretherketone composite membranes for fuel cells applications

Cristina Baicea, Vlad Ionut Luntraru, Ovidiu Gales, Stefan Ioan Voicu (svoicu@gmail.com)
University Polytechnica of Bucharest, Faculty of Applied Chemistry and Materials Sciences,
Str. Gheorghe Polizu 1-7, Bucharest, Romania

The increase of energy consumption and the problem of environmental protection represent enough reasons for new energy sources with a lower impact for environment. The fuel cells devices respond to these requests, due to their emissions and better yields. The synthesis and characterization of two different composite membranes, sulfonated polyetheretherketone-polyaniline and sulfonated polyetheretherketone-polypyrrole is presented. The ionic conductive properties of the polyaniline and polypyrrole will be used for giving and improving the conductive performances of the sulfonated polyetheretherketone membranes. The synthesis of both types of membranes starts from a SPEEK membrane followed by the polymerization of aniline or pyrrole inside the membrane pores in the presence of an oxidant. The use of sulfonated polyetheretherketone – polyaniline composite membranes for fuel cells application was previously reported in literature [1]. In order to increase the ionic conductivity of conductive polymers, the polyaniline was reversible functionalized with poly-styrene sulfonic acid and calmagite and the polypyrrole was functionalized with cerium sulfate and iron chloride. The water, methanol and ethanol fluxes through membrane was measured, the membranes were structurally characterized using SEM, FT-IR spectroscopy, thermal analysis and the ionic conductivity was evaluated by Electrochemical Impedance Spectroscopy.

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Functional finishing of linen fibrous supports using ZnO–MCT nanocomposites

Narcisa Vrinceanu*, Claudia Hristodor*, Eveline Popovici*, Florin Branza*, Diana Coman**,
Daniel Gherca*, Stefan Toma (narcisa.vrinceanu@ulbsibiu.ro)
"Al. I. Cuza" University of Iasi; "L. Blaga" University from Sibiu

A strong multidisciplinary is required by the increasing demand for multifunctional fabrics meaning approaches as well as the merging of the traditional scientific disciplines [1–3]. Finishing processes by means of nanoparticles has been the first commercial application on textiles. But these finishes are not washing resistant, due to poor fixing of these nanoparticles on the textile surface. Using functional polymer matrices as host molecules for nanoparticles will result in nanofinishings with improved bonding properties in fabrics and also impart desired wettability with different functional properties like self-cleaning, UV resistance, and flame retardancy which are unique characteristics of different nanoparticles. The present study investigates the efficiency of a grafting treatment using a cyclic oligosaccharide, β -cyclodextrin (i.e., monochlorotriazinyl- β -cyclodextrin).

The ZnO nanoparticles were prepared by a novel aqueous method and applied onto linen fabrics initially functionalized with a reactive derivative of a cyclic oligosaccharide, β -cyclodextrin (i.e., monochlorotriazinyl- β -cyclodextrin). Due to their characteristic molecular structure, cyclodextrin and its derivatives may form inclusion compounds with a wide range of guest compounds (nanofinishing agents). Grafting of the reactive compound on the cellulosic paper support was realized by a relatively simple pad dry-cure treatment, under mild conditions, while inclusion of the protective substances – by wet treatment with a guest solution. The treated supports were characterized by Fourier Transform-Infrared Attenuated Total Reflexion Spectroscopy (FT-IR ATR) and Scanning Electronic Microscopy (SEM).

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