



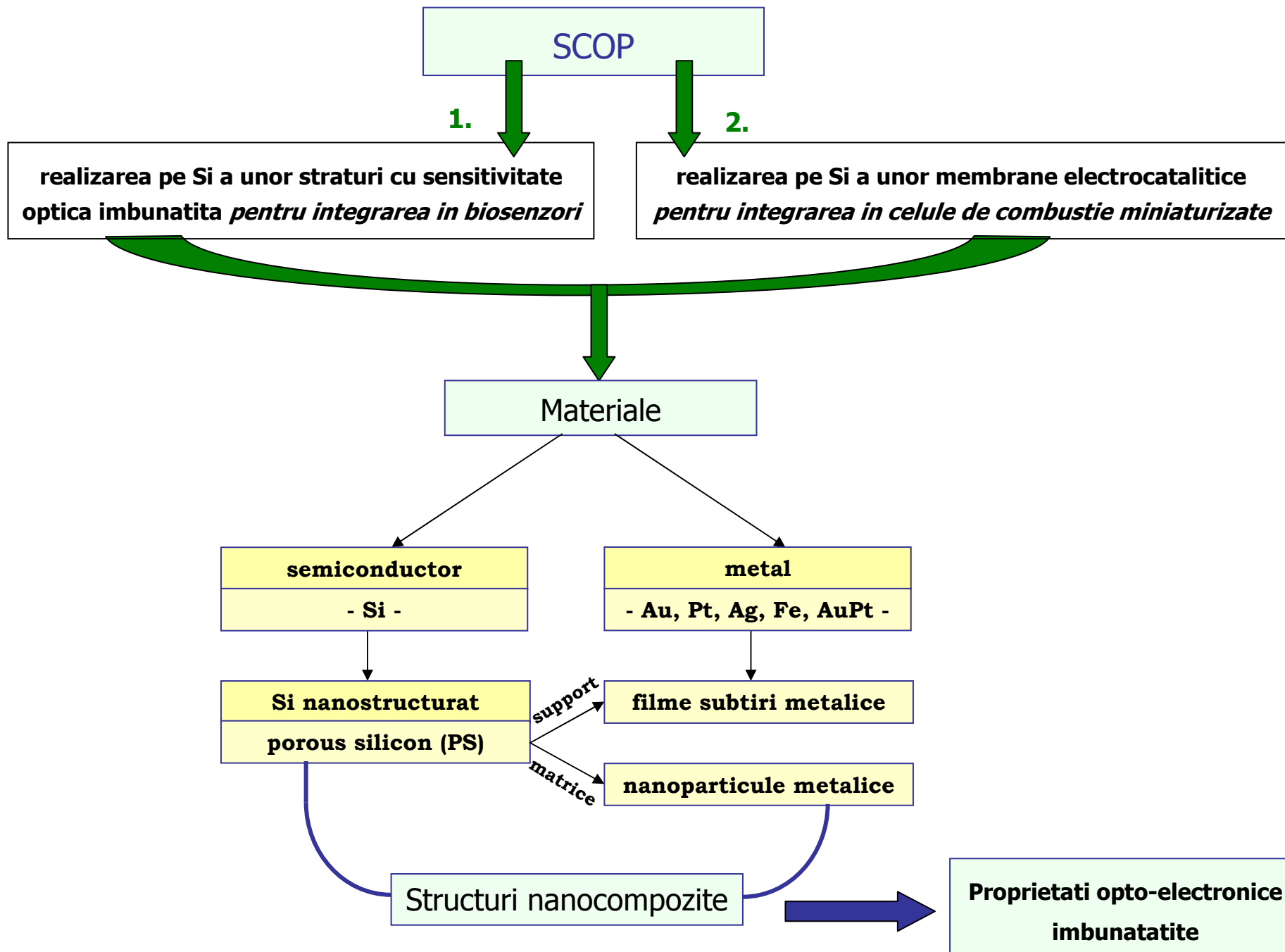
IMT-Bucharest

National Institute for Research and Development in Microtechnologies

Laboratorul de Nanotehnologii

Straturi nanocompozite metal / semiconductor

pentru integrarea in dispozitive opto-electronice



Morfologia PS – analize SEM

Phys. Adrian Dinescu: FE-SEM analyses (*Nova NanoSEM 630 system*)

Marimea porilor / fibrilelor depind de:

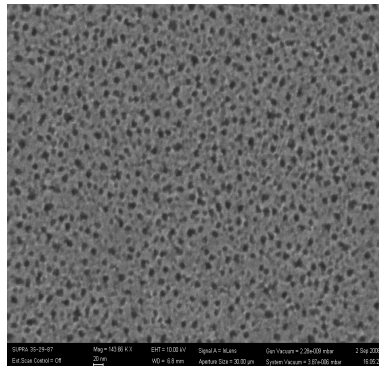
Substratul de Si

- tip si grad de dopare;
- orientare cristalografica.

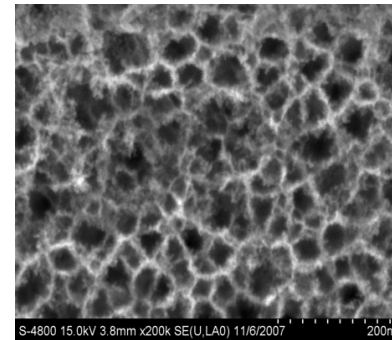
Parametrii de proces:

- electrolit;
- densitate de curent;
- conditii de iluminare.

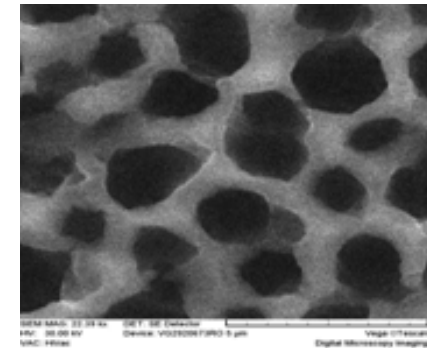
nano-PS (< 15 nm)



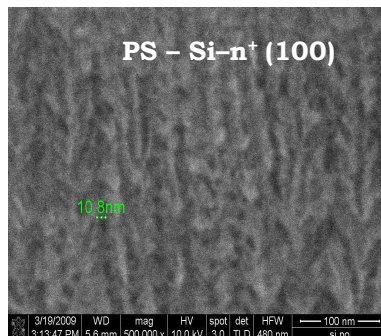
meso-PS (50- 100 nm)



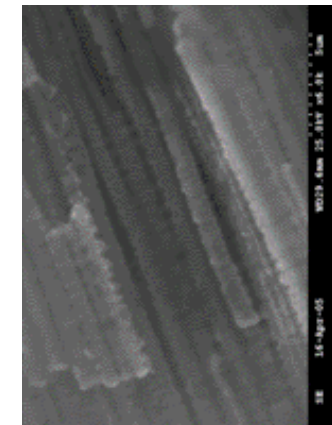
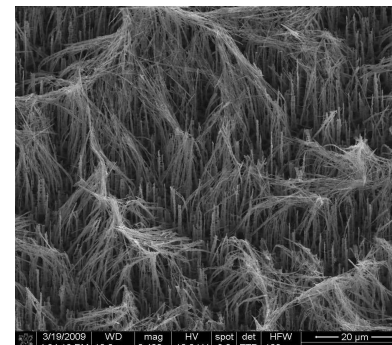
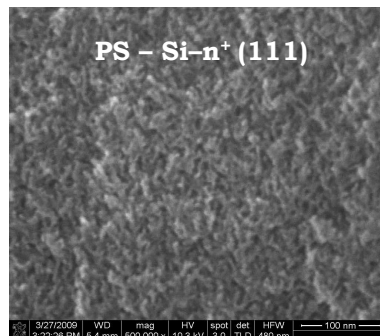
macro-PS (1- 2 μm)



PS – Si-n⁺ (100)



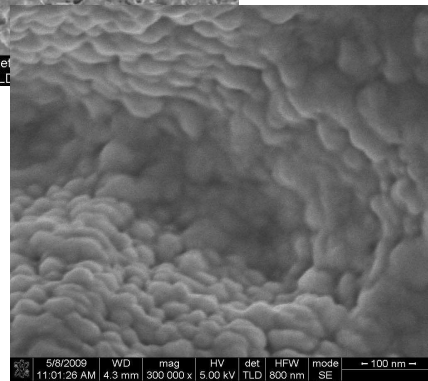
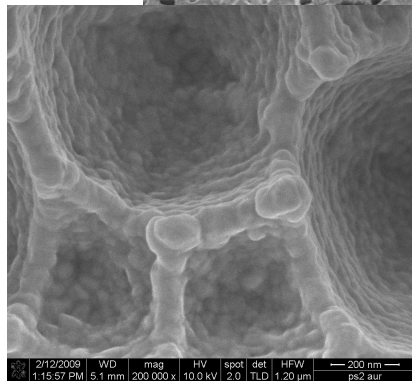
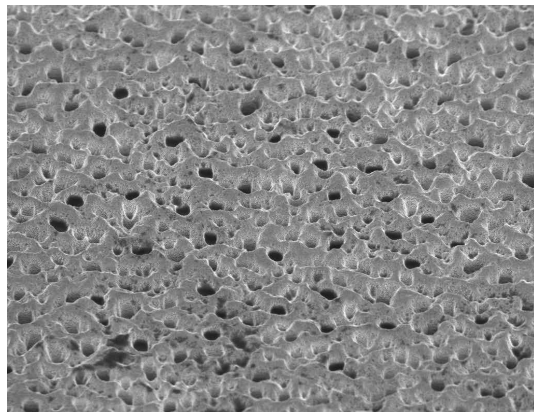
PS – Si-n⁺ (111)



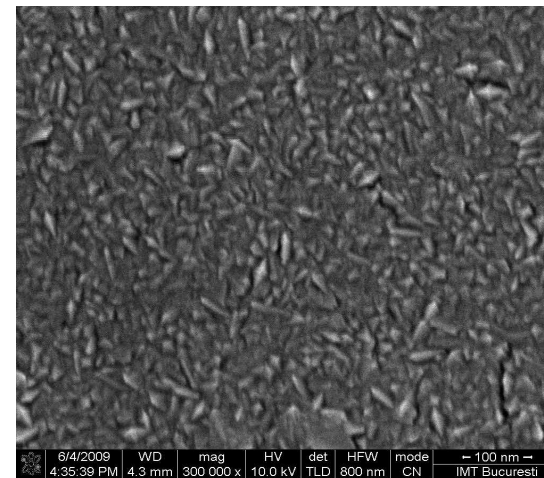
Morfologia straturilor nanocompozite – I

Filme metalice subtiri (NP-PVD) pe substrat de PS obtinute utilizand **metode fizice de depunere in vid**

filme subtiri Au (100 nm)
– cathodic sputtering system –



filme subtiri Pt (100 nm)
– E-beam high vacuum thin film deposition system –



OBSERVATII:

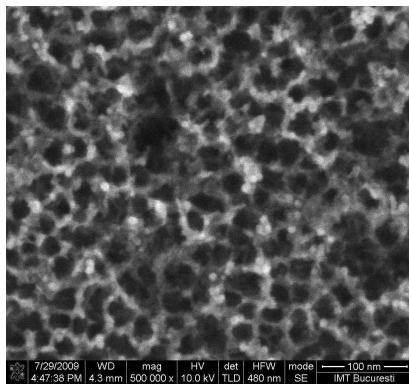
- utilizarea PS ca substrat creste aderenta si, in plus, determina nanostructurarea filmelor metalice

Morfologia straturilor nanocompozite – II

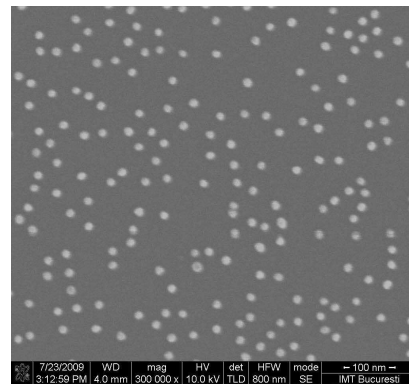
Nanoparticule metalice (NP-CD) distribuite pe / in matricea PS obtinute utilizand **proceduri chimice**

Au NPs

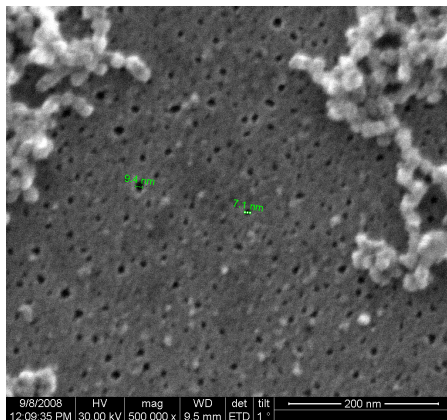
- solutie coloidala - 10nm NPAu;
- solutie precursor 0.2 mM HAuCl₄ (aqueous)



aqueous solution



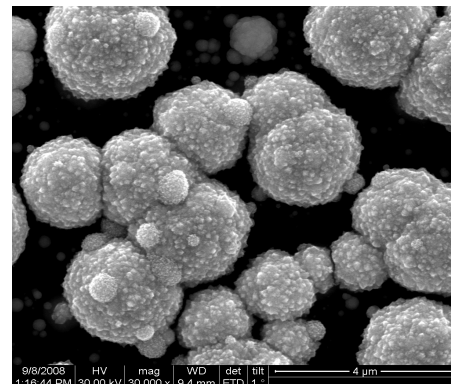
colloidal solution



Pt NPs

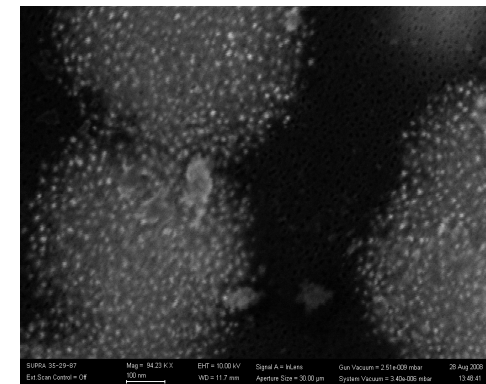
- solutie precursor 3.5 mM H₂PtCl₆ (aqueous or ethanolic)

Pt_{NP-CD} / nanoPS / Si

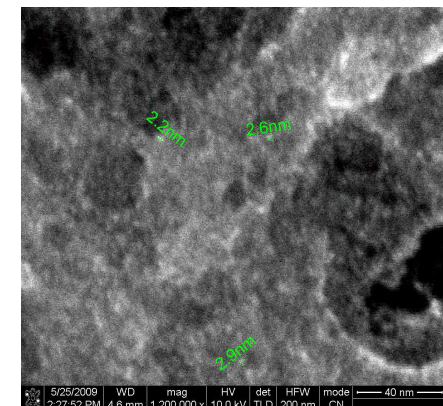
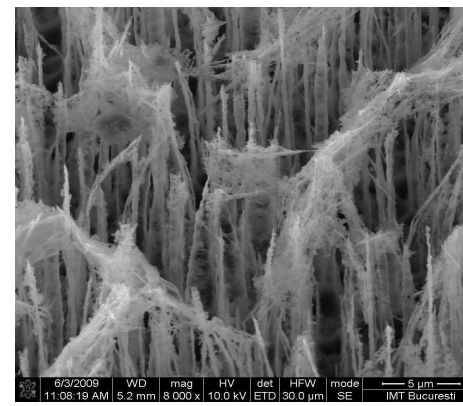


aqueous solution

Pt_{NP-CD} / mesoPS / Si



ethanolic solution



Analiza structurii cristaline a straturilor Au - PS

Phys. Mihai Danila: diferite tehnici de masura XRD (Rigaku Smartlab system)

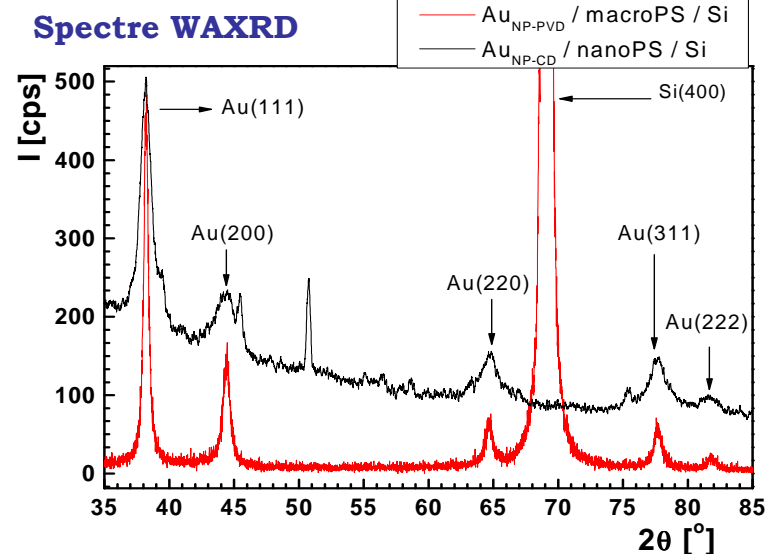
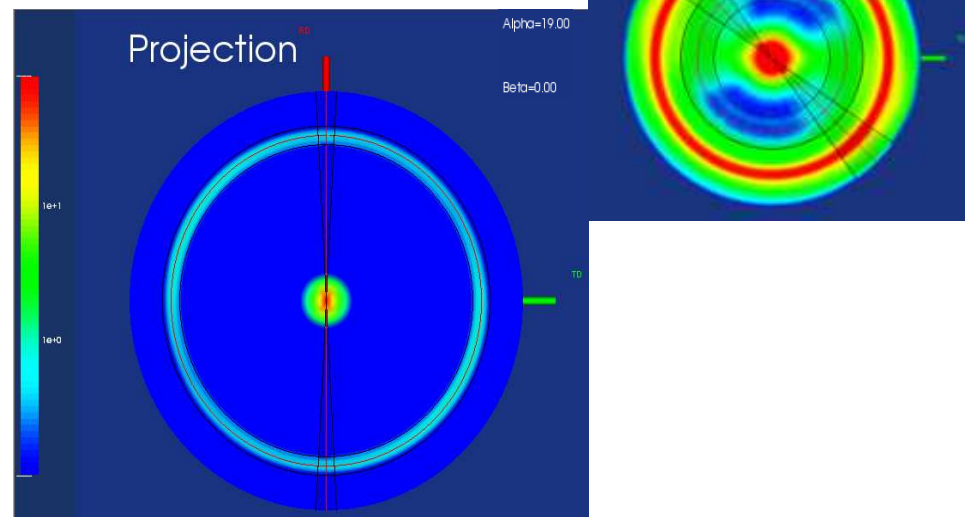


Figura de poli Au (111)



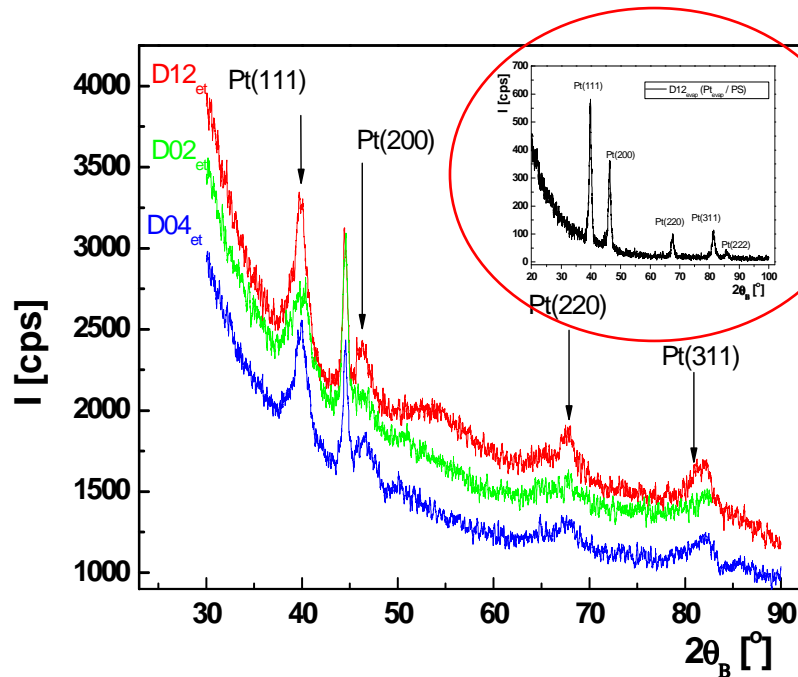
OBSERVATII:

- nanoPS (10 nm diametrul porilor) determina o texturare puternica (111) si un continut cristalin mai mare;
- spectrul WAXRD demonstreaza un raport mare intre intensitatea difractata de planele (111) si celelalte maxime - (200), (220), (311), (222), (400) - ale structurii cfc a Au, indicand o orientare preferentiala a NPs in principal pe plane de tip {111}

Referinte:

"Study of Nanocomposite Metal/Porous Silicon Material", M. Miu, I. Kleps, M. Danila, T. Ignat, M. Simion, A. Bragaru, **J. of Alloys and Compounds**, (Corr. proof, Av. online 20 January 2010);

Analiza structurii cristaline a nanoparticulelor de Pt in functie de natura suportului de PS

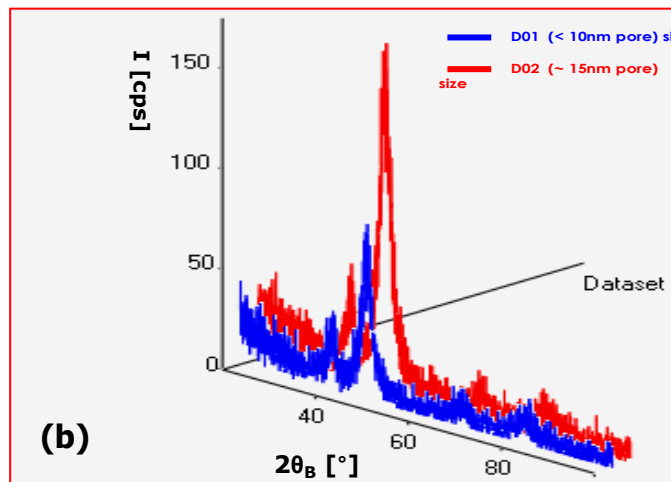


OBSERVATII:

Filmul metalic evaporat are un continut mai scazut de faza cristalina a Pt pentru ca intensitatile inregistrate sunt cel puțin 5 ori mai mici ca cele ale nanoPt

Nanoparticulele de Pt depuse pe membrana de **PS / Si - (111)** prezinta o texturare dominanta **(111)** in comparatie cu toate celelalte nano-ansambluri **Pt - PS** > confirma faptul ca procesul de cristalizare a Pt are loc initial in interiorul porilor si apoi continua pe suprafata

Cresterea dimensiunilor porilor membranei de la **10 nm** la **15 nm** conduce la cresterea marimii cristalitelor in directie paralela cu suprafata si la cresterea continutului de faza de Pt cristalina

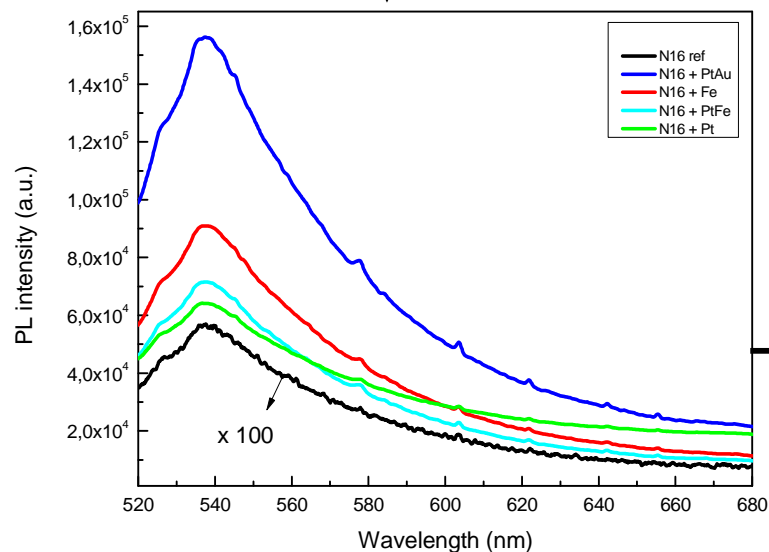


- utilizarea unui substrat de Si - (100) determina un continut cristalin mai mare si marimi medii mai mari ale cristalitelor de Pt;
- utilizarea unui substrat de Si - (111) determina o textura (111) mai pronuntata a particulelor de Pt

Bio-detectie optica – analize PL

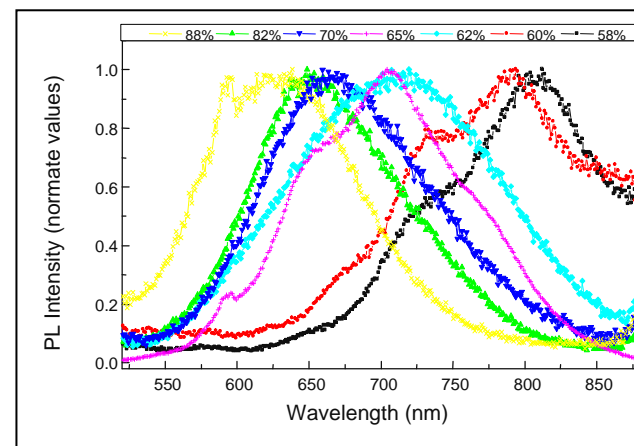
Single Photon Counting (SPC) FL spectra -
FLSP920 spectrometer (Edinburgh Instruments)

**Amplificarea fotoluminiscentei PS prin
depunerea MeNPs**



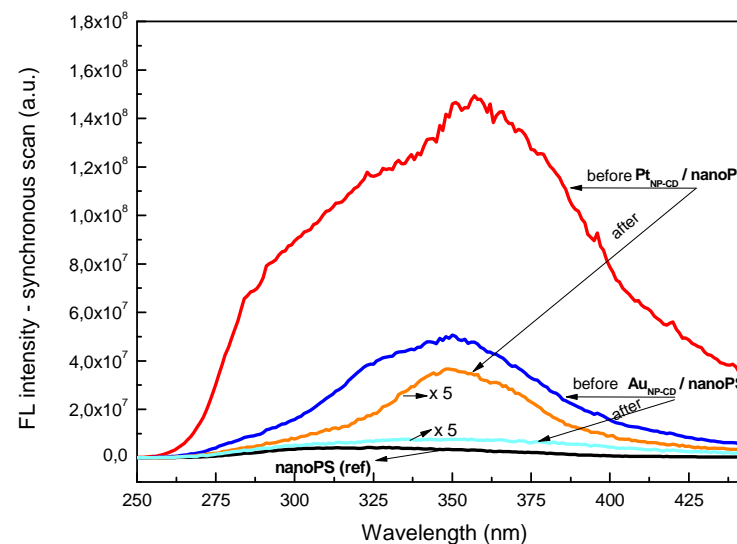
- Impregnarea matricei semiconductoare nanostructurate cu diferite MeNPs (Pt, Au, Fe) conduce la *amplificarea intensitatii emise*;
- observatie: MeNPs au efect numai asupra intensitii, care creste cu mai mult de doua ordine de marime, fara modificarea pozitiei maximului PL.

Spectre de fotoluminiscenta pentru straturi PS / Si-p
cu diferite porozitati (58% - 88%)



Spectrele sincrone de fluorescenta ($\Delta\lambda = 10nm$)

inainte si dupa expunerea structurilor
Pt_{NP-CD} / nanoPS si **Au_{NP-CD} / nanoPS**
in solutie 1% BSA in PBS



Referinte: "Metal – semiconductor nanoassemblies for improving of sensing efficiency", M. Miu, I. Kleps, F. Craciunoiu, T. Ignat, M. Simion, A. Dinescu, A. Bragaru, M. Danila, **ECS Transactions**, 25 (11) 45-55 (2009);

Bio-detectie – Substrat activ SERS pentru identificarea moleculelor

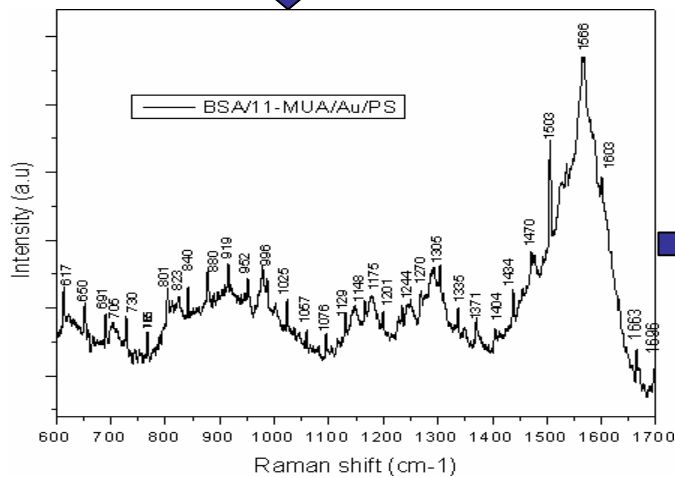
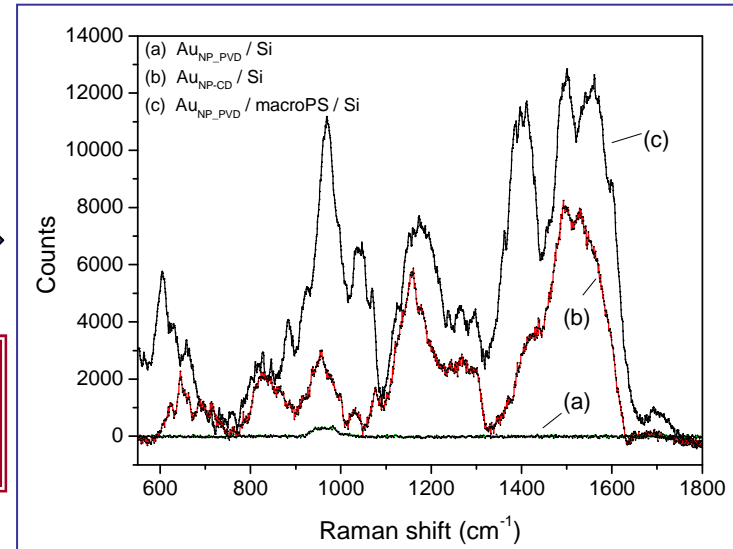
Dr Munizer Purica, Eng. Florin Comanescu - Raman spectroscopy system (*LabRAM HR 800* – Horiba Jobin Yvon)

Moleculele de tiol sunt auto-asamblate pe AuNP pentru a recunoaste o proteina data

Spectre Raman ale 11- MUA adsorbit pe diferite substraturi

OBSERVATIE:

Au_{NP-PVD}/macroPS este cel mai bun substrat pentru detectie SERS



Spectrul SERS al BSA pe SAM of thiols / AuNP-PVD / macroPS / Si

Referinte:

"Nanostructured Au/Si substrate for organic molecule SERS detection" T. Ignat, R. Munoz, I. Kleps, I. Obieta, M. Miu, M. Simion, M. Iovu, *Superlattices and Microstructures*, 46 (3), 451-460 (2009);

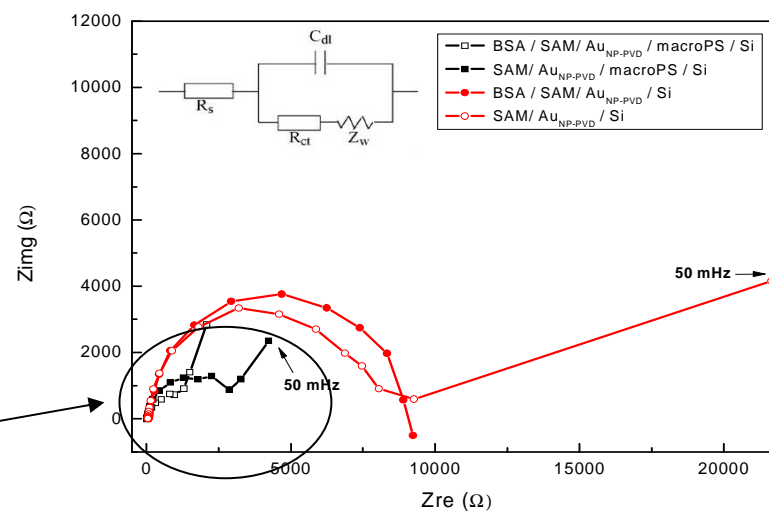
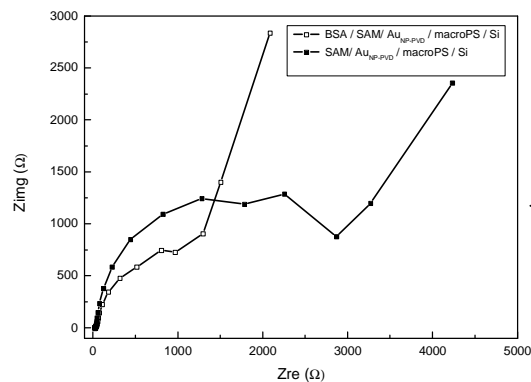
Bio-detectie electrochimica – spectroscopie de impedanta

PARSTAT 2273 system– Princeton Applied Research

Curbe Nyquist pentru masuratorile de impedanta Faradaica inainte si dupa interactia cu BSA utilizand ca elemente sensitive structurile:

$SAM / Au_{NP-PVD} / macroPS / Si$

$SAM / Au_{NP-PVD} / Si$



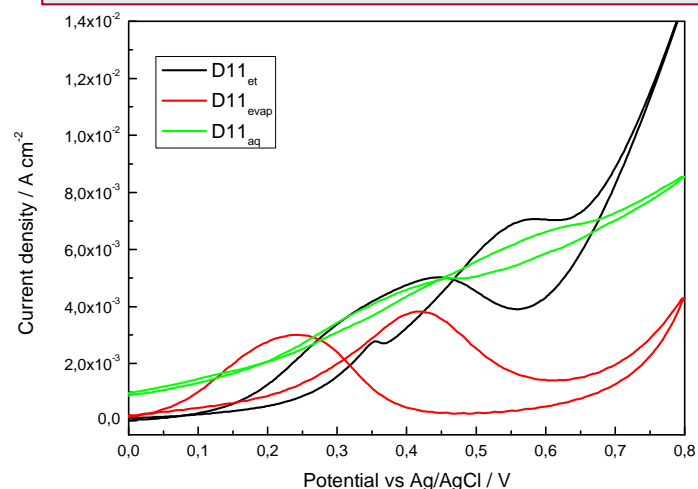
OBSERVATII:

- Utilizarea unui substrat nanostructurat pentru depunerea metalului conduce la cresterea suprafetei electrodului si implicit la aparitia unui numar mai mare de stari active > rezistenta de transfer a sarcinii ajunge la valori de 3 ori mai scazute pentru structurile Au - PS > modificarile in impedanta la adsorbția proteinei sunt mult mai vizibile (creste sensibilitatea) > actioneaza ca un senzor impedimetric

Referinte:

"Electrochemical characterization of BSA/11-mercaptoundecanoic acid on Au electrode", T. Ignat, M. Miu, I. Kleps, A. Bragaru, M. Simion, M. Danila, **Materials Science and Engineering B** xxx (2009) xxx-xxx;

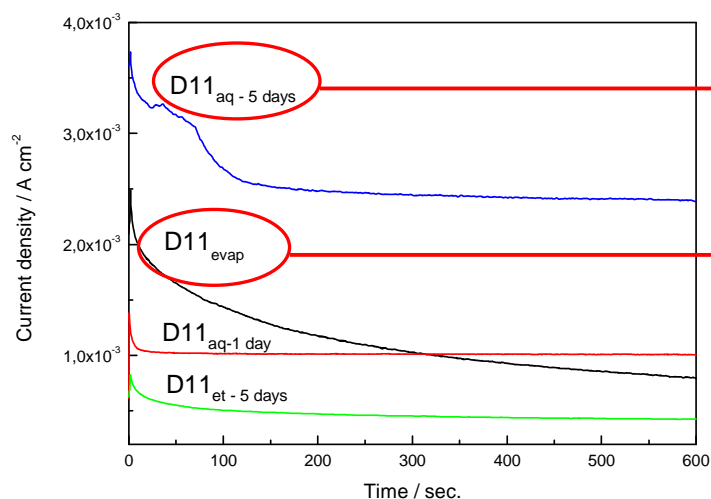
Analiza comportarii electrochimice a ansamblurilor nanocompozite PS - Pt



OBSERVATII:

Sistemele compozite **nanoPt / nanoSi** demonstreaza performante electrocatalitice bune in raport cu cantitatea mica de catalizator de Pt depus

Stabilitatea nanocatalizatorilor in timpul reactiilor electrochimice



Marirea timpului de stocare a probelor (cazul depunerii chimice) conduce la cresterea cantitatii de nanoparticule depuse si curentul inregistrat devine chiar mai mare decat cel al Pt evaporate.

Desi in valoare absoluta curentul inregistrat este mai mare, filmul subtire nanostructurat de Pt prezinta cea mai mare instabilitate in timp.

Stabilitatea nanoparticulelor de Pt dispersate in matricea de nanoSi

➤ speciile CO adsorbite pot fi ulterior oxidate si indepartate de pe nanocatalizatorilor de Pt datorita vecinatatii fibrilelor de Si si a starilor active de pe suprafata lor.

**Cronoamperometrie la potentialul de oxidare
~ 0.4V in solutie 1M CH₃OH + 1M H₂SO₄**

Referinte:

"Metallic - semiconductor nanosystem assembly for miniaturized fuel cell applications", M. Miu, M. Danila, T. Ignat, I. Kleps, F. Craciunoiu, M. Simion, A. Bragaru, A. Dinescu, **Superlattices and Microstructures**, 46 (1-2) 291-296 (2009);
„Electrocatalytic Activity of Platinum Nanoparticles Supported on nanoSilicon”, M. Miu, I. Kleps, M. Danila, T. Ignat, M. Simion, A. Bragaru, A. Dinescu, accepted for publication in **Fuel Cells** (2010);

CONCLUZII:



s-au realizat si s-au caracterizat morfologic / compozitional structuri nanocompozite metal - PS

s-a demonstrat ca nano-ansamblurile de tipul *nanoSi* / *nanoPt* determina:

➤ **cresterea senzitivitatii in biodetectia optica si electrochimica pentru integrarea in biosenzori;**

➤ **o activitate electro-catalitica eficienta in raport cu cantitatea de Pt depusa si in plus au o stabilitate mult mai buna in timpul reactiilor electrochimice pentru integrarea in celule de combustie miniaturizate.**